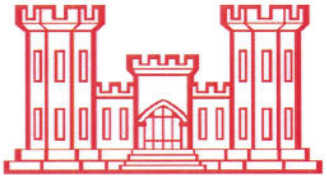
FINAL SITE-SPECIFIC FIELD SAMPLING PLAN

REMEDIAL INVESTIGATION, PART 1, AT ACID AREA 1

FORMER PLUM BROOK ORDNANCE WORKS
SANDUSKY, OHIO

Prepared for:



DEPARTMENT OF THE ARMY
NASHVILLE DISTRICT, CORPS OF ENGINEERS
NASHVILLE, TENNESSEE
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Prepared by:

JACOBS ENGINEERING GROUP, INC.
125 BROADWAY
OAK RIDGE, TN 37830

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COMPLETION OF INDEPENDENT TECHNICAL REVIEW

Jacobs Engineering Group, Inc. has completed the Final Site-Specific Field Sampling Plan for the Acid Area 1 Remedial Investigation Part 1: Site Characterization at the Former Plum Brook Ordnance Works, Sandusky, Ohio. Notice is hereby given that an independent technical review has been conducted that is appropriate to the level of risk and complexity inherent in the project, as defined in the Quality Control Plan. During the independent technical review, compliance with established policy principles and procedures, utilizing justified and valid assumptions, was verified. This included review of assumptions; methods, procedures, and material used in analyses; alternatives evaluated; the appropriateness of data used and level of data obtained; and reasonableness of the results, including whether the product meets the customer's needs consistent with law and existing Corps policy.

[signature]	Geologist	4/12/07
(Signature)	(Discipline)	(Date)

Independent Technical Review Team Leader and Team Members

(Signature)	(Discipline)	(Date)

Independent Technical Review Team Leader and Team Members

(Signature)	(Discipline)	(Date)

Independent Technical Review Team Leader and Team Members

Al Hardisty	Geologist	April 12, 2007
(Signature)	(Discipline)	(Date)

Jacobs Field Sampling Plan Addendum Author

CERTIFICATION OF INDEPENDENT TECHNICAL REVIEW

Responses to comments from the PBOW Team review are provided as appendices to the document and changes have been incorporated as appropriate.

All concerns resulting from independent technical review of the project have been considered.

Al Hardesty
(Signature)
(Project Manager)

April 12, 2007
(Date)

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LIST OF ACRONYMS AND ABBREVIATIONS

AA2	Acid Area 2
AA3	Acid Area 3
amsl	above mean sea level
AOC	area of concern
ASTM	American Society for Testing and Materials
bgs	below ground surface
°C	degrees Celsius
COC	contaminants of concern
DERP	Defense Environmental Restoration Program
DOD	U.S. Department of Defense
DPT	direct push technology
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
°F	degrees Fahrenheit
FID	flame ionization detector
ft	feet
gpm	gallons per minute
IDW	investigation-derived wastes
IT	International Technology Corporation
MDC	maximum detection concentration
MDL	method detection limit
MRL	method reporting limit
OVA	organic vapor analysis
PA	preliminary assessment
PAH	polynuclear aromatic hydrocarbon
PBOW	Plum Brook Ordnance Works
PBS	Plum Brook Station
PCBs	polychlorinated biphenyls
PID	photoionization detector
PRG	Preliminary Remediation Goal
QAPP	Quality Assurance Project Plan
QCP	Quality Control Plan
RBC	risk based criteria
RBSC	risk-based screening concentrations
RI	remedial investigation
SAIC	Science Application International Corporation
SAP	Sampling and Analysis Plan
SI	site investigation
SSFSP	Site-Specific Field Sampling Plan
SHP	Site-Wide Safety and Health Plan
SSHP	Site-Specific Safety and Health Plan
SWQAPP	Site-Wide Quality Assurance Project Plan
SVOC	semi-volatile organic compound
SWFSP	Site-Wide Field Sampling Plan
SWSAP	Site-Wide Sampling and Analysis Plan

TAL	Target Analyte List
TCL	Target Compound List
TNT	trinitrotoluene
USACE	United States Army Corps of Engineers
VOC	volatile organic compound

1.0 PROJECT DESCRIPTION

The U.S. Army is conducting investigations of the environmental impact at previously owned U.S. Department of Defense (DOD) properties. This work is being conducted by the U.S. Army Corps of Engineers (USACE) under the Defense Environmental Restoration Program (DERP). The Plum Brook Ordnance Works (PBOW) site, located in Sandusky, Erie County, Ohio, is a formerly used defense site under DERP. This Task Order is being managed and technically overseen by the Nashville, Tennessee USACE District Office. Jacobs Engineering (Jacobs) has been contracted to conduct Part 1 of a Remedial Investigation (RI) at Acid Areas 1 (AA1).

As an addendum to the PBOW Sitewide Sampling and Analysis Plan (SWSAP) (Jacobs 2004a), this Site-Specific Field Sampling Plan (SSFSP) has been prepared for the work to be conducted in support of the AA1 RI at PBOW. This SSFSP will be used in conjunction with the SWSAP (Jacobs 2004a) to ensure that work to be performed at this site will be of the quality required to satisfy the overall and site-specific project objectives. An addendum to the Site-Wide Quality Assurance Project Plan (SWQAPP) has been prepared and, in conjunction with this SSFSP, comprise the Site-Specific Sampling and Analysis Plan (SAP). A Site-Specific Safety and Health Plan (SSHP) has also been prepared separately for this remedial investigation that will be used in conjunction with the Site-Wide Safety and Health Plan (SHP)(Jacobs 2004b).

1.1 SITE HISTORY AND CONTAMINANTS

The acid production areas were in operation from 1941 to 1945 to produce oleum, sulfuric acid, and nitric acid for the manufacture of TNT. A records review was conducted by IT Corporation (IT) in preparation for a Site Investigation (SI) of the Acid Areas (IT 1998). The records review indicated that no previous investigations had been conducted at AA1. Available drawings of the site were used to identify some facility components. A review of the 1958 aerial photographs revealed several buildings and above-ground storage tanks at AA1. The majority of the site facilities were dismantled between 1958 and 1963. Buildings 302 Sulphuric Acid Concentration Plant, 308 Ammonia Oxidation Plant, and 310 are the only remaining original structures at the site.

Records were not available to describe operations at the PBOW Acid Areas. However, records are available which describe similar acid production operations at the Volunteer Army Ammunition Plant, Tennessee during the same time period. Acid production at all of the WWII-era ammunition plants are reported to have been fairly similar. The following sections summarize acid production at the Volunteer Army Ammunition Plant.

The acid areas produced various concentrations of acids for use at the batch TNT processing lines. The production area consisted of five main operations including:

- Weak nitric acid production
- Strong nitric acid production
- Reprocessing of spent sulfuric acid to produce strong sulfuric acid
- Oleum (sulfuric acid saturated with sulfur trioxide) production
- Mixed acid (strong nitric acid and oleum) production.

Weak nitric acid (60 percent nitric acid) was produced at the Ammonia Oxidation Process Building. Anhydrous ammonia used for the production of weak nitric acid was stored in tanks. Vapor compression to liquefy the ammonia was accomplished by compressors. Weak nitric acid was stored in area tank farms. The acid was then routed to the batch TNT process lines and to the Nitric Acid Concentrator facilities.

Strong nitric acid (95 to 98 percent nitric acid) was produced at the Nitric Acid Concentrator Buildings. The process involved mixing weak nitric acid with strong sulfuric acid (93 percent syllabic acid) for dehydration of the nitric acid. The resultant strong nitric acid was mixed with oleum (a mixture of sulfuric and sulfur trioxide) to produce mixed acid, which was used in the batch TNT nitration process. After the nitric acid and oleum were combined, the mixed acid product was approximately one-half nitric acid and one-half sulfuric acid. This mixed acid was used in lieu of strong nitric acid in the batch process lines because less expensive carbon steel piping could be used to convey it rather than the more costly stainless steel. Until needed, the mixed acid was stored in above-ground storage tanks.

The Sulfuric Acid Concentrator recycled sulfuric acid recovered from the TNT manufacturing process and the nitric acid concentrating process to yield strong sulfuric acid. The strong sulfuric acid was produced at two concentrations, 78 and 93 percent, and were used in the production of oleum and strong nitric acid, or shipped out as sales acid.

Oleum was used in the production of mixed acid or routed directly to the batch TNT process lines for use in the nitration process. The Oleum Plant included a process to melt sulfur using steam, which was then passed over a series of baffles to remove dirt before it was stored in a lined pit. The molten sulfur was pumped into the Oleum Plant, where sulfur dioxide was formed by burning the sulfur. The sulfur dioxide was subsequently oxidized by a vanadium pentoxide catalyst to produce sulfur trioxide. A 40-percent oleum-sulfuric acid was produced by absorbing the sulfur trioxide in weak sulfuric acid supplied by the Sulfuric Acid Concentrator operations.

Neutralized acid waste was discharged into an acid neutralizing pit, then transferred to a holding pond, and eventually discharged into a ditch.

Similar facilities have been identified at PBOW. AA1 consisted of eight buildings (Bldgs. 301-304, Bldgs. 306-308, and Bldg. 310), 43 above-ground storage tanks, and two rail lines (Figure 1-1). No information was obtained during the IT records review to indicate the type of process conducted at each building; however, identification of five storage areas was determined from the drawings: Oleum Storage (twelve tanks), Concentrating Mix Storage (six tanks), Sulfuric Acid Sales (twelve tanks), TNT Residual Acid Storage (five tanks), and Mixed Storage (8 horizontal tanks) as shown on Figure 1-1. Based on the location of the Oleum Storage, Sulfuric Acid Sales Storage, and Mixed Storage in close proximity to the rail line, the stored material was likely transferred directly to and from tanker cars or containers on a routine basis.

The SI of AA1 was conducted in 1998 by IT Corporation (IT) to determine the presence

of potential contaminants and to narrow the focus of any future sampling to specific contaminants of concern (COC). A total of fifteen soil borings were conducted at AA1, with one surface and one subsurface sample collected at each location. The SI identified surface and subsurface soil contamination above U.S Environmental Protection Agency (EPA) Region III Risk Based Criteria (RBC). Organic contaminants in surface soil exceeding the RBCs include the following:

- Nitroaromatics: 4-amino -2,6 - DNT
- Polychlorinated biphenyls (PCBs): Aroclor 1260

Subsurface soil samples were not analyzed for PCBs; therefore, it is not known whether PCBs are present at depth. There were no detected inorganic contaminants in surface or subsurface soil exceeding both the RBCs and the established background values. Contaminant distributions are presented in Figure 1-2.

One shallow overburden well and one bedrock well were installed at AA1. Groundwater samples were collected from both wells in November 1997 and May 1998. Sampling results indicate the presence of VOCs, SVOCs, and nitroaromatics in the bedrock groundwater at levels above USEPA Region 9 Tap Water Standards (October 2004). VOCs were detected in the overburden at levels above the USEPA Region 9 Tap Water Standards (October 2004).

1.2 SUMMARY OF SITE CHARACTERISTICS

1.2.1 Physical Setting

The AA1 site is located south of Maintenance Road and west of Taylor Road. The site physical features include an open field bounded by a drainage ditch to the south with scattered overgrowth throughout. Two railroad grades run east-west through the site: one on the southern perimeter and one through the northern portion of the site. The original service road encircles the site. The road is in fair condition and clear of vegetation. Buildings 302, 308, and 310 are the only remaining original structures at the site. All other buildings and tanks have been removed. NASA constructed a metal building between former Building 301 and Building 302. This building was formerly used by NASA as an incinerator, but is currently used for equipment storage.

The ground surface at AA1 is relatively flat, with minimal slope toward the drainage ditches to the north and south. Elevations at the site range from 637 to 639 ft above mean sea level (amsl). The drainage ditch to the south is located approximately 40 ft south of the service road and drains to the west, parallel to the site, discharging into Ransom Brook to the north of the site. This drainage feature has little relief adjacent to the site. The head waters of Plum Brook originate on site on the north central portion of the site and drain to the north. Plum Brook is approximately 30 to 40 ft wide and 15 to 20 ft deep just north of the AA1 site. During a site reconnaissance in May 2006, flowing water was present in both drainage features.

1.2.2 Site Geology

The AA1 site is situated on unconsolidated lacustrine deposits of glacial origin consisting of loamy fine sand, silts, and clays. These deposits are approximately 23 ft thick based on the boring information for bedrock monitoring well AA1-BEDGW-001. The Plum Brook Member of the Olentangy Shale subcrops beneath these unconsolidated deposits over the entire site. The thickness of this shale is approximately 15 ft in the center of the site, based on the boring information for the above referenced well. Thickness of the Plum Brook Shale should increase to the east-southeast and decrease to the north-northwest. The Plum Brook Shale is described as a blue, soft, fossiliferous shale containing thin layers of dark, hard, fossiliferous limestone. The Delaware Limestone underlies the Plum Brook Shale and averages 75 ft in thickness. The Delaware Limestone is described as a massive to thin-bedded, brown to gray, fossiliferous limestone and dolomite. Rock descriptions from nearby monitor well borings indicate fractures and naturally occurring oil are common in the Delaware Limestone.

1.2.3 Groundwater

Groundwater at AA1 has not been adequately characterized. One shallow overburden well and one bedrock well were installed, co-located at the northern boundary of the site. Existing well locations are presented on figures associated with Section 5.0 of this document. There is however, sufficient information from these wells and the *2004 Groundwater Data Summary and Evaluation Report* to estimate depths to shallow groundwater at the site and to estimate flow directions for both the shallow and deep groundwater. Based on the water level data provided in the 2004 groundwater report, shallow groundwater elevation at monitoring well AA1-GW002 was 637.5 ft amsl in May 2004, and 633.8 ft. amsl in August 2004. Depths to shallow groundwater ranges from 1 to 5 ft below ground surface. Based on other sites at Plum Brook, shallow groundwater flow is expected to flow toward the nearby drainage features.

Groundwater elevation contours for the Delaware Limestone indicate a linear feature running northeast-southwest through the PBOW in the vicinity of AA1, which acts as a preferential flow path. This feature is parallel to the bedrock strike and may represent a fracture system and/or karst development. Flow is toward the northeast along this feature. Groundwater elevations drop steeply toward this zone on either side. Because the AA1 site is located approximately 1000 to 1500 ft southeast of this feature, bedrock groundwater flows to the northwest.

1.3 SITE-SPECIFIC DEFINITION OF PROBLEMS

Chemical data obtained during the 1998 SI indicates that soil at AA1 has been impacted by contaminants originating from process systems previously operated at the site. Surface soil has been contaminated with PCBs and nitroaromatics. The 1998 SI identified the need for further investigation to define the nature and extent of soil contamination and to evaluate potential impacts to groundwater beneath the site and to surface water and sediment in the nearby drainage ditches. Sampling results from

adjacent areas of known contamination with similar contaminants have demonstrated impacts to both the shallow and bedrock groundwater.

2.0 PROJECT ORGANIZATION AND RESPONSIBILITY

2.1 KEY PROJECT PERSONNEL

The key Jacobs person responsible for project planning, control, and execution of the SAP is the Jacobs Project Manager, Mr. Al Hardesty, who also serves as the Technical Lead and Site Manager. Additional key personnel include: the Project Chemist, Mr. Lonnie Fallin; the Data Manager, Mr. Dave Greenberg; the Program/Project Quality Manager, Mr. Joe Petrilli; the Safety and Health Manager and Site Safety Officer, Mr. Sean Healey; and the Technical Reviewer, Mr. Steve Lampkins. The duties and responsibilities associated with these key Jacobs project positions are outlined in the Quality Control Plan (QCP) (Jacobs, 2006).

All field activities will be conducted in accordance with this Site-Specific FSP and the requirements of the SSHP (submitted under separate cover). Jacobs staff assignments for management of health and safety compliance are detailed in the SSHP.

Supplemental field support will be provided by Ms. Helen Owens of Streamborn Environmental as a subcontractor to Jacobs for analytical sampling tasks, including soil, sediment, surface water, and groundwater.

3.0 SCOPES AND OBJECTIVES

3.1 TASK DESCRIPTION

Investigations to be conducted at AA1 include characterization of groundwater, soil, sediment, and surface water. Project objectives consist of the following:

- Evaluate and use existing data appropriate for AA1
- Define site physical features and characteristics
- Determine the nature and extent of contamination in soil and groundwater
- Determine chemical characteristics of contamination
- Determine fate and transport of contamination
- Determine any site impact on the drainage features bounding the site
- Obtain site data of quality, quantity, and distribution appropriate for site characterization, risk assessment, and feasibility study

3.2 DATA QUALITY OBJECTIVES

Existing data for AA1 has been evaluated by Jacobs and considered for development of project data quality objectives (DQOs). Data collected at the site includes results from surface and subsurface soil samples, lithologic descriptions of subsurface soil collected from borings, and groundwater data from existing monitoring wells. These data have been considered in developing sampling strategies.

DQOs have been developed in accordance with the EPA Guidance for the *Data Quality Objectives Process* (EPA QA/G-4) (EPA 2000) and *Data Quality Objectives Process for Hazardous Waste Site Investigations* (EPA QA/G-4HW) (EPA 2000).

Part of the DQO process involves identification of a planning team responsible for development of objectives and implementation of decision rules during field activities. The planning team for investigations at PBOW consists of representatives from the U.S. Army Corp of Engineers – Nashville and Huntington Districts, the Ohio EPA, and Jacobs.

3.2.1 Conceptual Site Model

Based on site data, contaminants associated with the former acid production areas have impacted the surface soil. Data collected during the 1998 SI indicate the presence of surface soil contamination exceeding RBCs for PCBs and nitroaromatics. In general, the highest concentrations of contaminants are associated with former buildings and process facilities. Minimal contamination was identified in the undisturbed areas between facilities. Eleven of the fifteen soil borings completed at AA1 were within the footprint of former facilities or immediately adjacent to facilities. The remaining four soil

borings were completed in undisturbed areas between facilities or along the rail line. Seven of the eleven locations associated with facilities showed contamination exceeding the RBCs. Only one of the four locations in undisturbed areas had contamination exceeding the RBCs.

All but one of the RBC exceedances was for PCBs (Figures 1-2). Since PCBs were not analyzed for subsurface soil, conclusions regarding downward migration of contaminants cannot be made. However, PCBs were rarely detected in the subsurface at Acid Area 2 and Acid Area 3.

Additional contaminant migration may have occurred, impacting groundwater, surface water and sediment. These potential processes will be evaluated during this investigation. Groundwater contamination may have occurred from precipitation and infiltration processes, resulting in leaching of contaminants from the soil. Potential groundwater pathways include vertical migration into the bedrock aquifer and lateral migration of shallow groundwater toward the drainage ditches. Potential surface water and sediment contamination may have occurred from shallow groundwater recharge to the drainage system, by overland flow and transport of contaminated soil particles during heavy precipitation, or spreading of surface contamination by vehicles and equipment used during former operations.

3.2.2 Problem Statement – Step 1

Soil samples collected during the 1998 SI were screened against the EPA Region III RBCs. Soil contamination exceeding RBCs is present at the site. Soil in the vicinity of several former process facilities has not been investigated. It is unknown whether site contaminants have migrated to groundwater, surface water, or sediment. This investigation will seek to determine the presence of site contaminants in soil at other former site facilities that have not been evaluated, to further define the extent of contamination at those facilities which have been identified as impacted based on the SI data, and to determine the presence or absence of PCBs in soil at depth. In addition surface water, sediment, and groundwater data to be collected during this investigation will help to address human health and environmental risk concerns.

3.2.3 Decision Statements – Step 2

The following decision statements were developed based on the question of whether site contaminants present a risk to human health and the environment requiring remediation:

- Conduct further investigation of soil near process facilities not characterized during the 1998 SI.
- Determine the physical characteristics of the unconsolidated glacial/lacustrine deposits and the underlying bedrock including thickness, lithologic classification, and hydraulic properties.
- Determine the physical characteristics of the shallow and bedrock groundwater including depth, gradient, and flow direction.
- Determine whether shallow and bedrock groundwater has been impacted by site

contaminants.

- Determine whether surface water and sediment in the drainage ditches have been impacted by site contaminants.

3.2.4 Decision Inputs – Step 3

The majority of the decision inputs involve the collection of new environmental data, the focus of this DQO process. This step will address inputs and considerations critical to the collection of new data.

Region 9 Preliminary Remediation Goals (PRGs) for soil and OEPA approved site-wide background values for inorganics in soil will be used to evaluate the level of contamination at the sites. These PRGs are discussed in Section 3.2 of the Site-wide Field Sampling Plan (SWFSP) (Jacobs 2004a). At the conclusion of this investigation, the need for additional sampling will be determined and negotiated based on the initial findings and the results of the risk assessment. Tables 3-3 through 3-7 of the Site-Specific Quality Assurance Project Plan (QAPP) present the PRGs to be used for the soil investigation.

EPA Region 9 PRGs for groundwater and established site-specific background values for inorganics in groundwater will be used to evaluate whether additional investigation of site groundwater is warranted. PRGs are addressed in Section 3.2 of the SWFSP (Jacobs 2004a). Tables 3-8 through 3-13 of the QAPP present the PRGs to be used for the groundwater investigation.

In addition to the PRGs, laboratory method reporting limits (MRLs) and laboratory method detection limits (MDLs) are also critical to effective evaluation of site data. MRLs for the contracted laboratories are compared to PRGs in Tables 3-3 through 3-13 of the Site-Specific QAPP.

Data needs for the risk assessment and feasibility study must also be considered as decision inputs. Sufficient data for a given population of soil will be obtained to perform a statistically based risk assessment.

Existing site data will be used to develop sampling strategies for new environmental data. Groundwater monitoring wells will be located based on an evaluation of chemical data from nearby wells and water level contour maps developed as part of the 2004 site-wide groundwater study (Shaw 2005). Use of existing chemical data for surface and subsurface soil for incorporation into the risk assessment will be based on review of the Data Validation Summary Report and Laboratory Analytical Data Summary Report from the 1998 SI.

3.2.5 Study Boundaries – Step 4

AA1 has some man-made and natural spatial boundaries related to the soil investigation, consisting of the service road which encircles all sides of the former acid production facilities and the drainage ditches bounding the south side. These features form the study boundaries.

The vertical boundary for the delineation of soil contamination is defined as the upper ten ft of soil, consistent with the DQO Process for Hazardous Waste Sites, EPA, 2000.

Temporal boundaries identified for the investigation include seasonal fluctuations in the shallow groundwater that may directly affect the surface water and groundwater investigations. Seasonal fluctuations may affect the surface water discharge in the drainage feature north of the site.

3.2.6 Decision Rules – Step 5

Placement of soil borings have been will be biased toward former acid production facilities such as buildings, storage tanks, and disturbed areas as defined on the 1958 aerial photographs. The decision as to whether to install shallow groundwater monitoring wells will be dependant on the presence of sufficiently conductive materials in the shallow subsurface, which will be determined by the placement of eight temporary peizometers. If there is not sufficient conductive material in the overburden, then locations for the shallow monitoring wells will be evaluated and discussed with USACE – Nashville District. If contaminants exceeding the USEPA Region 9 PRGs are detected, then additional investigation activities may be conducted such as a risk assessment or additional delineation sampling.

3.2.7 Decision Errors – Step 6

Because this initial phase of investigation is intended to identify areas of contamination at the site, decision errors relate primarily to accurate identification of all former process facilities. The 1958 aerial photos and available engineering drawings are the only resource available for identifying these facilities. It is possible that some facilities are not represented on the 1958 photos, having been dismantled or areas restored prior to 1958.

3.2.8 Design Optimization – Step 7

The sampling design optimization will include the following elements:

- The soil sampling strategy and locations will be based on identification of process facilities and features that were not previously investigated or data gaps for areas adjacent to formerly investigated facilities.
- Lithologic borings and piezometers will be installed to further define the conceptual site model.
- Co-located surface and subsurface soil samples will be collected from borings installed in the vicinity of identifiable site features.
- Monitoring wells will be installed in both the overburden material and bedrock to allow for sampling and evaluation of impacts to groundwater. The final well location design will be based on preliminary data obtained during the soil investigation and peizometer monitoring.
- Co-located surface water and sediment samples will be collected from the drainage ditches bounding the site.

Soil boring locations have been selected to fill data gaps or provide additional characterization at major operational facilities, based on the 1958 aerial photographs (Figure 3-1). Rationale for each location is as follows:

- SB-16: Provide additional coverage on west side of SA Tanks
- SB-17: Fill data gap at possible transfer location adjacent to the Oleum Storage Tanks
- SB-18: Provide additional coverage on east side of SA Tanks
- SB-19: Provide additional coverage on west side of Oleum Tanks
- SB-20: Provide additional coverage on east side of Oleum Tanks
- SB-21: Fill data gap on west side of building 308
- SB-22: Fill data gap on south side of building 308
- SB-23: Fill data gap on northeast corner of building 308
- SB-24: Provide additional coverage in center of TNT Residual Acid Tanks
- SB-25: Fill data gap on north side of Strong Mixed Acid Facility
- SB-26: Fill data gap on south side of Strong Mixed Acid Facility
- SB-27 and SB-28: Provide additional coverage at the Mixed Storage Tanks
- SB-29: Fill data gap on east side of Building 303
- SB-30 and SB-31: Provide additional coverage at Concentrating Mix Tanks
- SB-32: Provide additional coverage on south side of Concentarting Mix Coolers
- SB-33 through SB-36: Fill data gap around the perimeter of Building 302
- SB-37 and SB-38: Fill data gap on north and east sides of Building 301

3.3 APPLICABLE REGULATIONS/STANDARDS

Applicable regulations and standards are addressed in the SWSAP.

3.4 PROJECT SCHEDULE

Each investigation conducted under this SWSAP will involve a similar set of project milestones and project activities, which will have a project-specific schedule. Project activities include the following components:

Draft Work Plans	5 January 2007
Final Work Plans	16 March 2007
Field Investigation (Soil, Surface Water, Sediment – Part 1)	16 – 28 Apr 2007
Field Investigation (Soil, Surface Water, Sediment – Part 2)	14 – 22 May 2007
Well Installation and Development (Bedrock)	11 – 21 June 2007
Well Installation and Development (Shallow)	9 – 20 July 2007
First Quarterly Groundwater Sampling	30 July 2007 – 9 August 2007
Second Quarterly Groundwater Sampling	5 – 13 November 2007

Draft Site Characterization Report	29 March 2008
Final Site Characterization Report	28 June 2008

4.0 NONMEASUREMENT DATA ACQUISITION

Non-measurement data acquisition for this investigation includes the use of existing data collected from prior investigations at AA1. Analytical data from soil samples collected at the AA1 during the 1998 SI are intended for use in the risk assessment.

5.0 INVESTIGATION METHODOLOGIES

This chapter describes the methodologies and procedures to be followed for the Remedial Investigation, Part 1 at AA1. The investigation activities will include:

- Groundwater monitoring well installation, development, and sampling
- Aquifer testing/hydraulic properties
- Soil borings with associated soil sampling
- Surface soil sampling
- Surface water and sediment sampling
- Land surveying

Sampling locations for these activities are presented in Figures 3-1 and 5-1. All investigation activities will be conducted in accordance with the Site-Wide SAP. A copy of the Site-Wide SAP will be kept in the field at all times for reference purposes during all field activities.

5.1 GEOPHYSICAL SURVEYS

Geophysical surveys are not planned as part of this investigation.

5.2 SOIL GAS SURVEY

Soil gas surveys are not planned as part of this investigation.

5.3 GROUNDWATER

A groundwater investigation will be conducted at AA1 to acquire data relative to groundwater level, groundwater flow, hydraulic conductivity, and impacts related to site contaminants. This investigation will include the installation of eight temporary piezometers, the installation and development of three overburden wells and three bedrock wells, and the collection of groundwater samples from four existing nearby wells and all newly installed wells.

5.3.1 Monitoring Well Installation and Development

Eight temporary piezometers will be installed around the perimeter of the site (Figure 5-1). Data from these piezometers will further define the site conceptual model and flow of shallow groundwater at the sites. The piezometer data will also be used to evaluate the feasibility of installing permanent shallow monitoring wells. Piezometers will be placed outside of the footprint of any former building or tanks to avoid additional migration pathways for site contaminants.

Borings for the piezometers will extend to the top of bedrock and will be installed using direct push technology (DPT). During installation, lithologic information will be recorded to further define the conceptual site model. Well casing and screens will be constructed of 1-inch diameter PVC tubing. The annulus will be filled with clean sand to 1 ft bgs. Bentonite chips will be used to form a surface seal to minimize infiltration of surface water. Screen lengths will be approximately 10 to 15 ft in length extending from total depth to 10 ft bgs. Each piezometer will have a removable PVC cap. All piezometers will be removed and abandoned at the end of the investigation, approximately 2 to 3 months after installation. Borehole abandonment will be performed as specified in the SWSAP.

Six monitoring wells will be installed in accordance with the SWSAP, consisting of three overburden wells and three bedrock wells (Figure 5-1). Co-located overburden and bedrock wells will be installed at each of three locations: one upgradient, one downgradient, and one in the center of the site. Co-located wells will be placed within 10 to 25 ft of each other. Upgradient and downgradient bedrock well locations will be based on water level contour maps provided in the 2004 Groundwater Data Summary and Evaluation Report (Shaw 2005).

Borings for bedrock wells will be performed with an air-rotary rig. Borings will be continuously cored to allow for adequate descriptions of bedrock material, including the identification of water yielding zones. Bedrock wells will be screened in the Delaware Limestone, with the screen placement covering the best water-yielding zone nearest the top of the formation, with a minimum depth of 50 feet for the bottom of the well screen, based on observation of the cores and cuttings. Overburden wells will also be continuously sampled for lithologic characterization, with screen placement covering the best water-yielding zone nearest the surface, based on lithologic conditions. Screen lengths will be sized to fit a single discreet water bearing interval and will not exceed 10 ft in length, as specified in the *State of Ohio, Technical Guidance for Well Construction and Groundwater Protection, Appendix VI, Monitoring Well Design and Installation,* 2000.

Well materials will consist of 2-inch ID schedule 40 PVC flush thread casing and screen. Well screen slot sizes will be 0.010 and filter pack material will be 20/40 sand. Boreholes for shallow well installation will be a minimum of 4 inches in diameter larger than the casing diameter to allow for 2 inches of filter pack and annular material on all sides of the screen and casing. Boreholes for shallow wells will be advanced with 6.25-inch hollow stem augers. Boreholes for the bedrock wells will be advanced using a CME 85 rig equipped with a 94mm rock coring system. Centralizers will be used for wells deeper than 30 ft and will be spaced at 20 ft intervals. Centralizers will not be placed closer than 10 ft above the screened interval. All well materials will be emplaced using cased-hole methods.

Well locations may be adjusted within a radius of 100 ft to account for significant differences in shallow groundwater flow directions. If adjustments are made, well pairs will not be moved to a point such that the deep well is no longer upgradient or downgradient of the site. If piezometer information should indicate that shallow and bedrock groundwater flow paths are at or near right angles to one another, consideration will be given to disassociate the two wells. However, the shallow and deep

wells in the center of the site will remain co-located. Any decisions to change locations beyond 100 ft or to disassociate the well pairs will be made by the DQO planning team. Newly acquired site information will be provided to the team for review prior to implementing any changes.

During the installation of bedrock wells, special care will be taken to avoid cross-contamination of the bedrock groundwater. Following installation and pressure grouting of the surface casing, all borehole fluids will be pumped from the well. Clean potable water will be placed in the surface casing and measured for several minutes to confirm that the surface casing seal at the bedrock interface is sound. All water will again be pumped from the casing prior to advancement of the rock core.

Well development for all permanent wells will be conducted in accordance with the SWSAP.

5.3.2 Water Level Monitoring

Water level monitoring will be conducted on all newly installed wells and existing wells on a quarterly basis prior to sampling activities. Temporary piezometers will be measured a minimum of once per week during the soil investigation and monitoring well installation.

5.3.3 Groundwater Sampling

Groundwater samples will be collected from all newly installed wells and existing wells AA1-GW002, AA1-BED-GW001, MK- MW19, and MNTA-BEDGW-001, in accordance with the SWSAP. Samples will be analyzed for target compound list (TCL) volatile organic compounds (VOCs), SVOCs, target analyte list (TAL) metals, nitroaromatics, and PCBs. Samples will be collected quarterly (every three months) for a minimum of two rounds. The need for additional rounds will be evaluated after receiving analytical data from the first two rounds. The first round of sampling will include both filtered and unfiltered TAL metals. Filtering will be conducted in the field. Water quality parameters will also be collected as specified in Table 3-1 of the Site-Specific QAPP. Groundwater samples will be collected from the upgradient wells first, then the downgradient wells, followed by the wells located in the center of the site. QC samples will be collected as specified in the Site-Wide SAP and the Site-Specific QAPP

Groundwater sampling will be conducted starting with the areas assumed to be least contaminated to the areas assumed to be most contaminated. All sampling and purging equipment (pumps, tapes, and any reusable discharge hose) will be decontaminated before use and before each successive use in accordance with the decontamination procedures discussed in section 5.4.5 of the Final Site-Wide SAP. Collection of groundwater samples will be documented in the Monitor Well Purging Form and Groundwater Sampling Field Data Form.

Sampling of newly installed monitoring wells will take place no sooner than 14 days after well development has been completed. All equipment used to purge wells and collect

samples will be protected from ground surface contact and contamination by use of clean plastic sheeting. The following procedures will be followed when collecting groundwater samples from all monitoring wells:

- The well will be checked for proper identification and structural integrity.

- After unlocking the well and removing the well cap, a PID will be used to measure the concentration or organic vapors at the top of casing and in the breathing zone. If readings are above background, safety precautions outlined in the SHP and SSHP will be followed.

- The depth to water will be measured using a decontaminated water level indicator, then the volume of water to be purged will be calculated. The purge volume will be based on 3 well screen volumes, which will include the saturated filter pack around the well screen.

- Where recharge rates permit, the well will be purged by an appropriate submersible sampling pump to remove three screen volumes. Low flow purging will be performed at a rate that allows for stabilization or gradually rising water levels, prior to, and during sampling. Efforts will be made to minimize the amount of drawdown while establishing the appropriate purge rate. Water levels will be monitored continuously during purging and sampling and will be recorded every 10 minutes along with the other water quality parameters.

- During purging and sampling, field measurements of pH, temperature, ORP, DO, turbidity, and conductivity will be performed every ten minutes utilizing an in-line flow-through cell. Sampling will not be performed until temperature and pH stabilize at +/-1°C and +/- 0.2 respectively, ORP stabilizes at +/- 10mV, specific conductivity stabilizes at +/- 3%, and DO and turbidity stabilize at +/- 10% for three consecutive readings.

- Groundwater samples will be collected using a submersible sampling pump and in-line sampling filters.

- Sample containers will be labeled with appropriate identifying information (location, date, time, condition, added preservatives, etc.). The preprinted labels will be provided by the field sampling crew leader. Each sample will be logged in a field notebook at the time of collection. Sample containers of appropriate volume and composition will be prepared in advance to ensure the collection of sufficient volumes for all specified analyses.

- The samples will be collected in the order of priority as VOC, SVOC, nitroaromatics, metals, and, lastly, other analytes as required for individual projects.

- Samples for volatile analysis will be collected in screw-cap, septum-top glass vials and filled so that there are no air bubbles present to allow volatilization.

- Samples for metals analysis will be collected in two separate containers; one will be filtered and the other will not be filtered. Samples will be filtered according to the

following procedures:

- The water sample will be filtered at the well site utilizing in-line disposable filters with a 0.45-micron filtering capacity or equivalent. Analysis for Mn II and Fe II will be performed in the field using a HACH or equivalent field test kit.

- All sample containers will be transferred to a cooler chest (kept at 4 degrees Celsius (°C)] and delivered to the laboratory in sufficient time so that specified holding times are not exceeded.

5.3.4 Field Hydraulic Conductivity Testing

Slug tests will be performed on all newly installed permanent monitoring wells in accordance with the SWSAP.

5.4 SURFACE AND SUBSURFACE SOIL SAMPLING

Soil sampling will be conducted to further characterize the site. Locations have been selected to fill data gaps as described in section 3.2.8. Soil borings will be conducted at the site using DPT methods for the collection of surface and subsurface soil samples (Figure 3-1). Soil samples will be collected at the surface from 0.5 to 1.5 ft bgs, and from the subsurface at three to five ft bgs at 22 locations. One additional boring (SB-37) will be installed with soil sampling limited to the surface soil only, due to budget constraints, as shown on Figure 3-1. All soil borings and sample collection will be conducted in accordance with the SWSAP. All samples will be analyzed for VOCs, SVOCs, nitroaromatics, TAL metals and PCBs. QC samples will be collected as specified in the Site-Wide SAP and the Site-Specific QAPP.

5.5 SURFACE WATER AND SEDIMENT SAMPLING

Prior to conducting surface water and sediment sampling, a site reconnaissance will be performed to identify all surface water features at the site and the associated drainage patterns. Based on a preliminary site walk in May 2006, there are at least five separate drainage features around the perimeter of the site. Information obtained during the site reconnaissance will be used to determine sampling locations. An addenda to this plan will be submitted for team review, which will contain an updated surface drainage map with sampling locations and rationale.

Co-located surface water and sediment samples will be collected from 15 locations. Sample locations will include an upstream sample and two downstream samples prior to convergence with any other surface water tributaries. Sampling will be conducted during base flow conditions, preferably no sooner than 24 hours following any major precipitation events determined to significantly impact discharge rates.

All samples will be collected in accordance with the SWSAP. Surface water and sediment samples will be analyzed for VOCs, SVOCs, nitroaromatics, PCBs, and TAL metals. QC samples will be collected as specified in the Site-Wide SAP and the Site-Specific QAPP

5.6 OTHER MATRICES

No other matrices are planned for this investigation.

5.7 LAND SURVEYING

Land surveying will be conducted for all sampling locations and newly installed monitoring wells in accordance with the SWSAP.

6.0 FIELD OPERATIONS DOCUMENTATION

Field documentation will be conducted in accordance with the SWSAP.

7.0 SAMPLE PRESERVATION, PACKING, AND SHIPPING

Sample preservation will be conducted in accordance with the SWSAP. Refer to Tables 3-1 and 3-2 of the Site Specific QAPP for analysis to be performed, sample containers, preservative, and holding times for each of the matrix types.

8.0 INVESTIGATION-DERIVED WASTE MANAGEMENT PLAN

The management, characterization, and disposal of investigation-derived waste (IDW) will be conducted in accordance with the SWSAP.

9.0 FIELD ASSESSMENT/INSPECTION PROCEDURES

9.1 QUALITY CONTROL

Quality control procedures will be conducted in accordance with the SWSAP. Daily calibration will be performed per the manufacturer's specifications and will be documented in the log book and on the appropriate calibration forms. If there are equipment failures, replacement units will be shipped to the site the following morning by the vendor. Jacobs' vendor will be Scientific Sales Inc, out of Oak Ridge, Tennessee.

9.2 SAMPLING APPARATUS AND FIELD INSTRUMENTATION

The following equipment will be used during this investigation:

- Horiba or YSI flow-thru cell
- Horiba or YSI calibration fluid
- PH buffer solution
- Peristaltic pump (surface water sampling – non-VOC)
- Bladder pump
- Bladder pump controller and compressor
- Water level indicator
- Teflon coated disposable tubing
- Stainless steel well slug
- In-situ well datalogger – 1 inch diameter
- Generator
- Extension cords
- Five gallon buckets with lids
- Core boxes
- Munsell Soil Color Charts
- Encore sampler
- Stainless steel bowls and spoons

- Photoionization detector (PID)/ Flame ionization detector (FID)
- Calibration Gas
- Canned Air
- Deionized Water American Society for Testing Materials (ASTM) Type II
- Liquinox
- Decon brushes
- Plastic sheeting
- Wooden stakes
- Flagging tape
- Tape measure
- 5-lb hammer
- Coolers
- Thermometers
- Personal protective equipment: hard hat, safety glasses, tyvek, nitrile gloves

10.0 VARIANCES, NONCONFORMANCES, AND CORRECTIVE ACTION

Variance and nonconformance procedures presented in the SWSAP will be followed.

11.0 REFERENCES

IT Corporation (IT), 1998, *Site Investigations of Acid Areas, Former Plum Brook Ordnance Works, Sandusky, Ohio*, December 1998.

Jacobs, 2004a, *Site-Wide Sampling and Analysis Plan*, May 2004

Jacobs, 2004b, *Site-Wide Safety and Heath Plan*, May 2004

Jacobs, 2006, *Quality Control Plan for Remedial Investigation Part 1: Acid Area 1, Former Plum Brook Ordnance Works, Sandusky, Ohio*, October 2006

Shaw Environmental, Inc., 2005, *2004 Groundwater Data Summary and Evaluation Report, Former Plum Brook Ordnance Works*, April 2005.

State of Ohio, *Technical Guidance for Well Construction and Ground Water Protection*, 2000

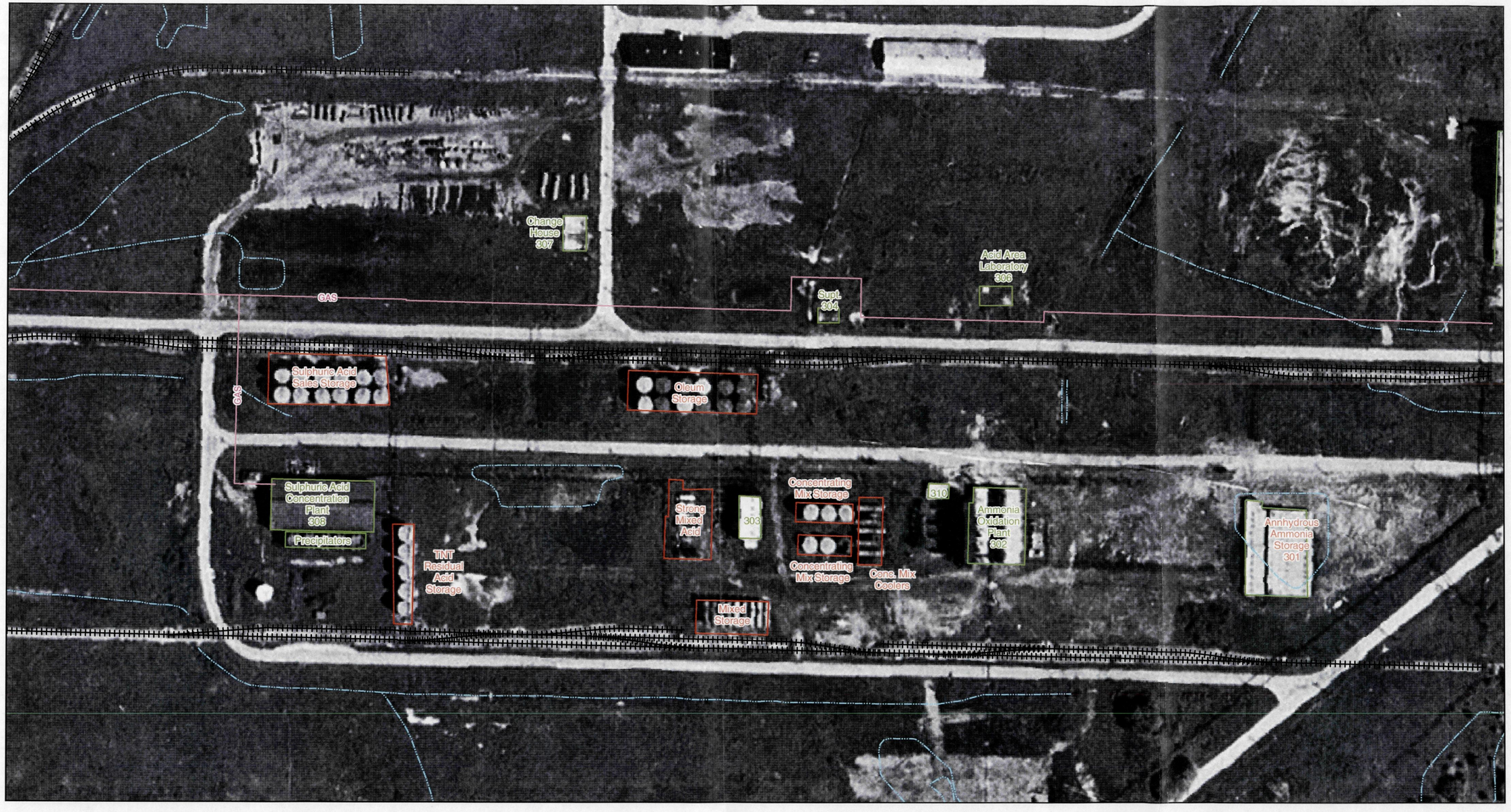
U.S. Environmental Protection Agency (EPA), 2002, *Drinking Water Standards and Health Advisories*, Office of Water, Washington, DC, Summer 2002.

U.S. Environmental Protection Agency (EPA), 2003, *Risk-Based Concentration Table, July-December 1995*, Jennifer Hubbard, EPA Region III, April 16, 2003.

U.S. Environmental Protection Agency (EPA), 2000, *Guidance for the Data Quality Objectives Process (EPA QA/G-4), 1994*

U.S. Environmental Protection Agency (EPA), 2000, *Data Quality Objectives Process for Hazardous Waste Site Investigations* (EPA QA/G-4HW), 2000

Figures



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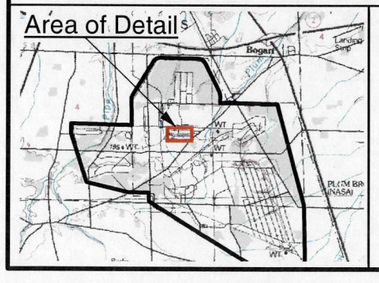


Legend

- Storage Tank Areas from Engineering Drawings
- Buildings from Engineering Drawings
- Creek, Ditch, Conveyance
- Railway

200 100 0 200
Feet

N

Notes: *Aerial Photography from 1958.*
Data mapped to Ohio State Plane North NAD83, map units are feet.

JACOBS

Acid Area 1 — 1958
Aerial Photography

Plum Brook Ordnance Works
Sandusky, Ohio

01/18/07 LKD S:/GIS/Projects/Plumbrook/Projects/AA1_Draft_SAP/ArcMap/Acid_Area1_1958.mxd

Figure 1-1

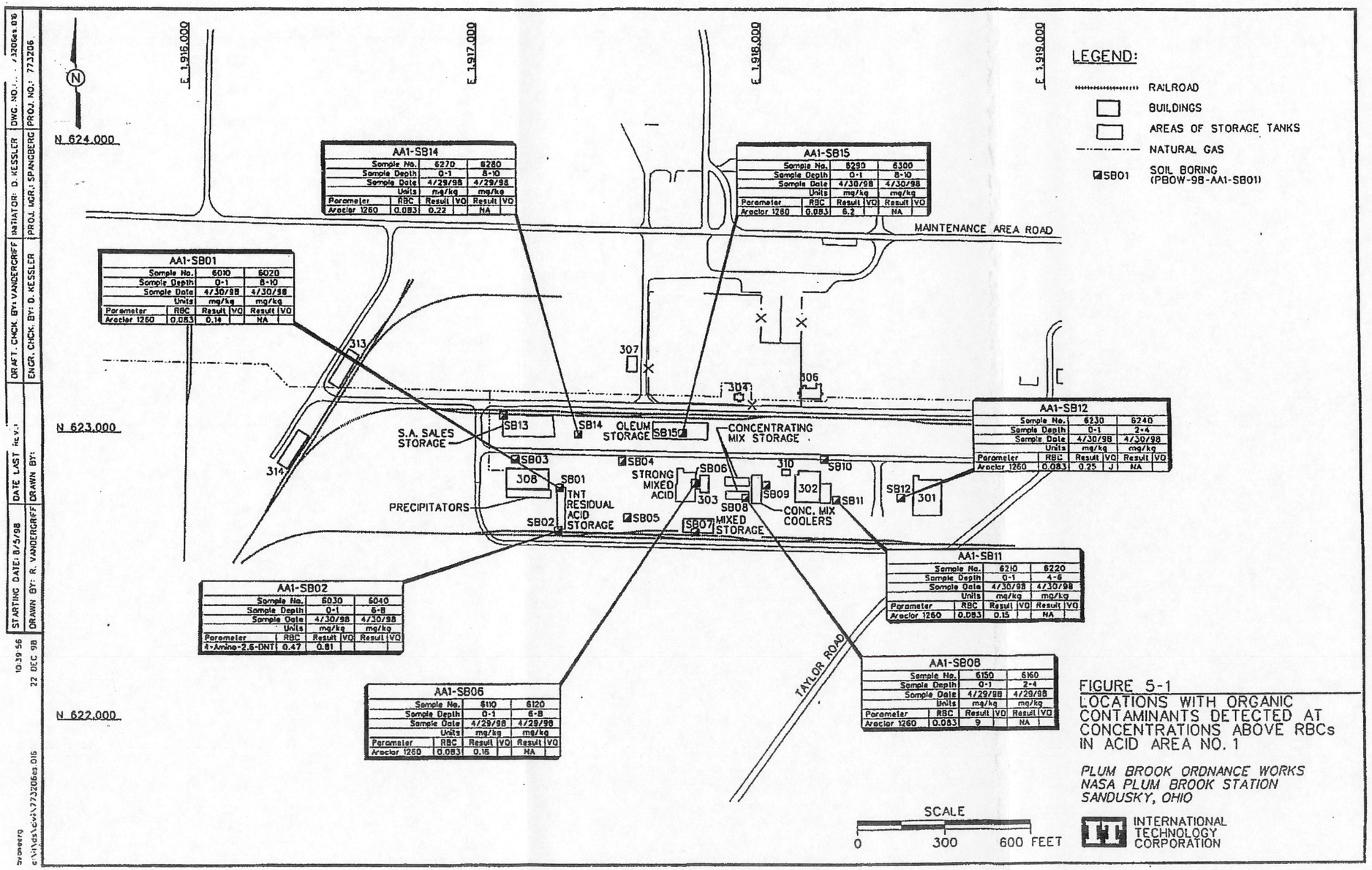
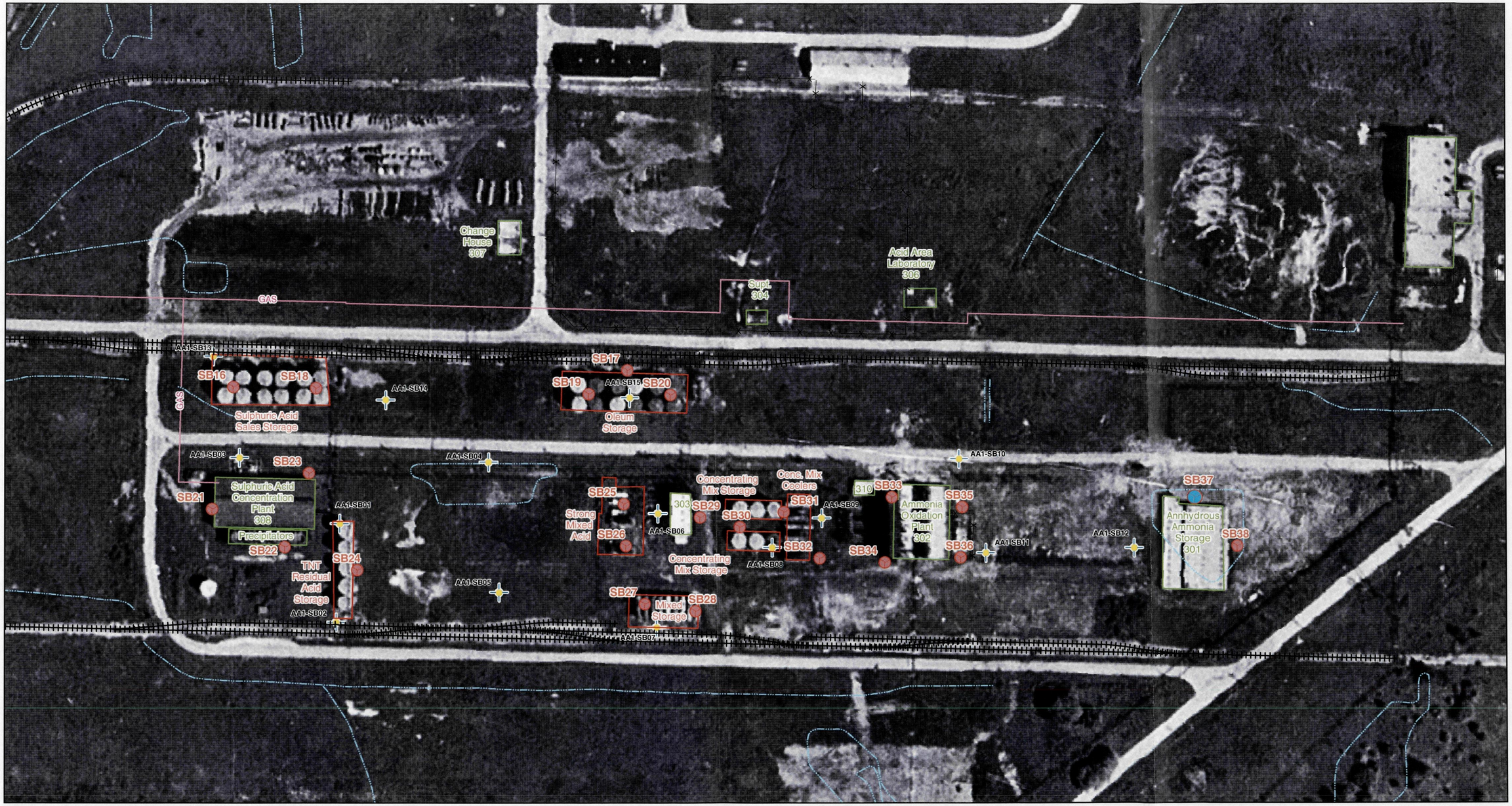


Figure 1-2 Acid Area 1 Contaminant Distribution



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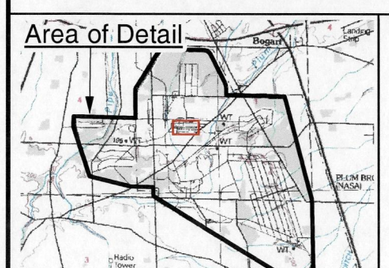


Legend

- Storage Tank Areas from Engineering Drawings
- Creek, Ditch, Conveyance
- Buildings
- Railway
- 1998 SI Soil Borings
- Proposed Soil Boring
- Proposed Surface Soil Only

0 50 100 200
Feet

N

Notes: *Aerial Photography from 1958.*
Data mapped to Ohio Stateplane North NAD83, map units are feet.

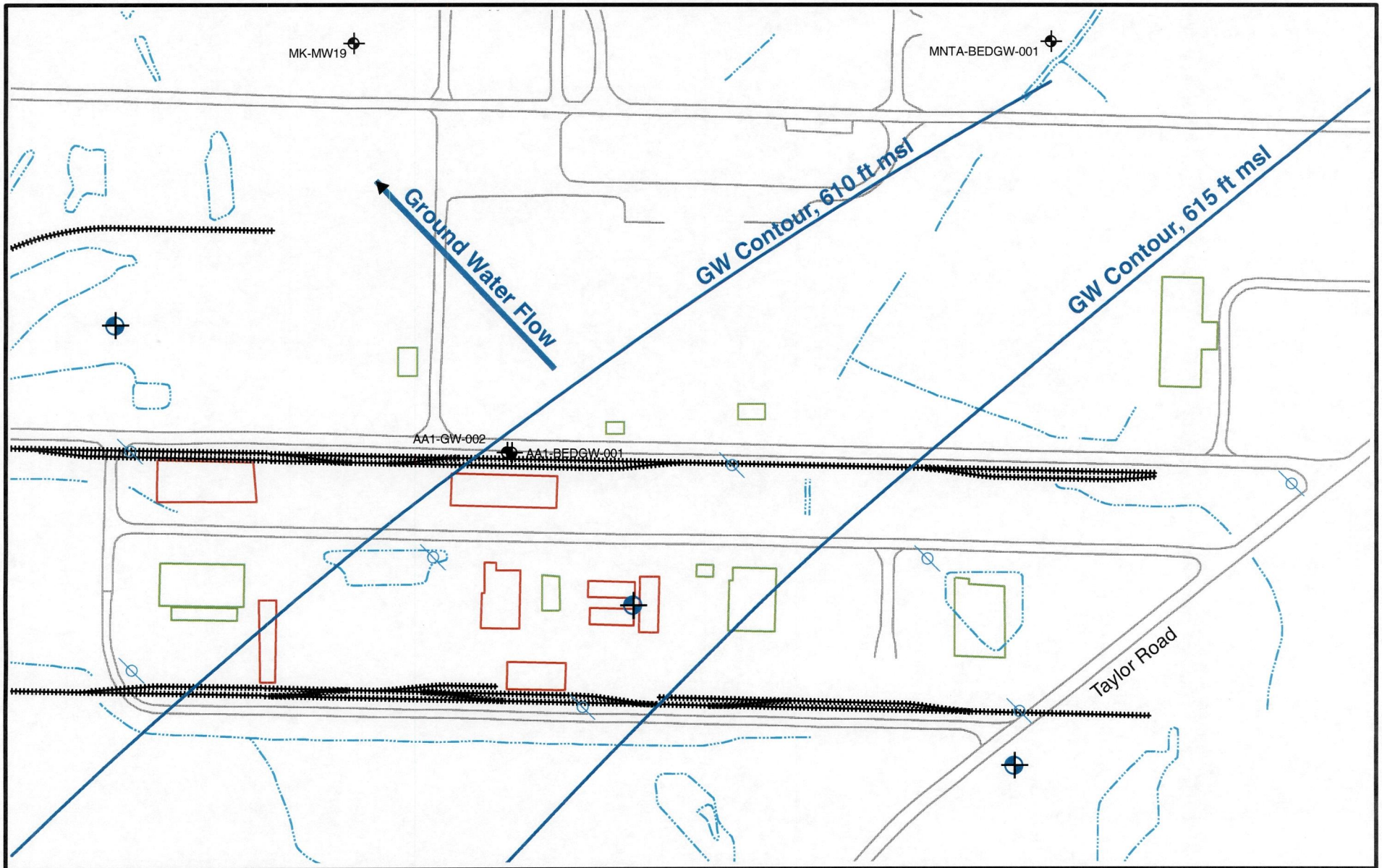
JACOBS

Acid Area 1
Soil Boring Locations

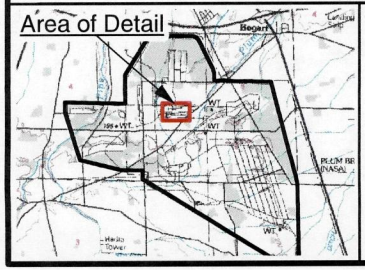
Plum Brook Ordnance Works
Sandusky, Ohio

4/11/07 LKD Y:/GIS/Projects/Plumbrook/Projects/AA1_Draft_SAP/ArcMap/AA1_Borings.mxd

Figure 3-1



Area of Detail



Legend

- Storage Tank Areas from Engineering Drawings
- Creek, Ditch, Conveyance
- Buildings from Engineering Drawings
- Railway
- Existing Monitoring Wells
- Proposed Piezometers
- Proposed Monitoring Wells

0 100 200 400
Feet

N

Notes:
Data mapped to Ohio State Plane North NAD83, map units are feet.

JACOBS

Acid Area 1 Groundwater Sampling Locations

Plum Brook Ordnance Works
Sandusky, Ohio

01/18/07 LKD S:/GIS/Projects/Plumbrook/Projects/AA1_Draft_SAP/ArcMap/AA1_GW_SW.mxd

Figure 5-1

Appendix A

Appendix A
Response to Comments

SUBJECT: Response to review comments for the Draft Sampling and Analysis Plan, Remedial Investigation, Part 1, at Acid Area 1, Former Plum Brook Ordnance Works (PBOW), Sandusky, OH, February 2007, Prepared by Jacobs Engineering Group, Inc., Contract Number DACW62-03-D-0004-0007

Reviewer: John Weaver, OEPA, Geology / Hydrogeology

1. **Jacobs Engineering Group, Inc. (Jacobs) proposes to install 8 piezometers across Acid Area 1 (AA1) and into the shallow overburden. Additionally, 3 pairs of co-located shallow overburden and bedrock monitoring wells will be installed at AA1. Monitoring wells will be installed in upgradient and downgradient positions as well as one pair centrally located within the unit. Ohio EPA has no exceptions to the proposed piezometers/monitoring well locations at AA1.**

Response: Comment noted

2. **All monitoring well installation, water level measuring, and ground water sampling techniques specified in Section 5.3 of the February 2007 Draft Site-Specific Field Sampling Plan (SAP) are appropriate. Jacobs is reminded that land surveying of the monitoring wells should include ground surface elevation, top of casing elevation, and northing/eating coordinates.**

Response: Elevation surveys of all monitoring wells will include the parameters as requested.

3. **Jacobs proposes to sample 10 monitoring wells at AA1 quarterly for at least two rounds to determine the rate, extent, and concentrations of hazardous waste constituents in the shallow overburden and bedrock (Delaware Limestone) ground water zones. Samples will be collected from existing shallow)overburden) wells MK-MW19, AA1-GW-002, and three proposed wells and existing bedrock wells MNTA-BEDGW-001, AA1-BEDGW-001, and three proposed wells. Samples will be analyzed for at least volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), polychlorinated biphenyls (PCBs), nitroaromatics, and total metals. Dissolved metals will be collected during the initial round only.**

   Ohio EPA is unclear if two rounds of sampling means two total rounds on a quarterly basis during one calendar year or the collection of samples on a quarterly basis for a period of two years (Section 3.1.3, page 3-2 of the QAPP).

Response: Groundwater sampling will be performed twice, once in July 2007 and again November 2007.

4. **While not explicitly stated in the SAP, Ohio EPA assumes that Jacobs will compare ground water analytical results to USEPA Region IX preliminary remediation goals (PRGs) similarly at Acid Areas 2 and 3.**

Response: Region 9 PRGs are discussed in Section 3.2.4.

5. **While not explicitly stated in the SAP, Ohio EPA assumes that Jacobs will generate**

soil boring, well construction, well development, and ground water sampling logs in support of the investigation at AA1.

Response: Section 6 addresses field documentation, which references the Site-wide SAP. The Site-wide SAP includes requirements for the requested information.

SUBJECT: Response to review comments for the Draft Sampling and Analysis Plan, Remedial Investigation, Part 1, at Acid Area 1, Former Plum Brook Ordnance Works (PBOW), Sandusky, OH, February 2007, Prepared by Jacobs Engineering Group, Inc., Contract Number DACW62-03-D-0004-0007

Reviewer: Carol Lee Dona, USACE - CX , Process Engineering

Field Sampling Plan (FSP)

Comment # 1:p. 1-1: The text references a 1958 aerial photo and refers to the Volunteer Army Ammunition Plant for Plant operating procedures but no language was found describing the operating time period of the Site. Please include.

Response: The text has been revised to include the period of operation for the acid production facility.

Comment # 2, p. 1-1: Is there any evidence that source areas of oleum remain, particularly near the Oleum Plant?. Please discuss with respect to the stability of oleum and the history of the Site.

Response: The former mixed acid production facility was dismantled between 1958 and 1963. The text has been revised to include additional history.

Comment #3: p. 1-3: Please include the nitrate concentrations in the discussion of the results form the groundwater sampling in November 1997 and May 1998. This is pertinent information given the apparent large volumes of nitric acid used/manufactured at the Site.

Response: Nitrogen was non-detected in both the shallow and bedrock wells.

Comment # 4, p. 5-3: Recommend that nitrate as a potential site-related compound be pointed out as an analyte that will be included in the water quality parameter sampling.

Response: Section 5.3.3 indicates that water quality parameters will be collected which includes nitrates.

Comment # 5, General: No groundwater purging and sampling procedures or references to the same were found in the FSP. Please include the procedures, including water quality parameters and the water quality stabilization criteria for collecting samples. (Note: even if the procedures can be referenced in another document, please include a summary of the procedures in this document).

Response: The text from the Site-wide SAP has been provided in the text.

Reviewer: Chung-Rei Mao, USACE - CX Chemistry

Comment # 1: Page 1-3, 1st paragraph: Please reconcile the inconsistency between the 2nd bullet, which states Aroclor 1260 was detected in surface and subsurface soil, and the following sentence, which states subsurface soil samples were not analyzed for PCBs.

Response: The text was revised to reflect only surface soil.

Comment # 2: Page 3-4, Section 3.2.7: Suggest that the project-specific "tolerable decision errors" on Type I and II errors of project-specific hypothesis tests, as discussed in step 6 of the DQO process in EPA guidance document QA/G-4, be discussed. This information is needed to determine the acceptance criteria for Measurement Quality Indicators, i.e., the minimum requirements on data precision and bias.

Response: This is addressed in the Final Site-wide QAPP.

Comment # 3: Page 5-3, Section 5.3.3: Please justify the need of both filtered and unfiltered TAL metals for the first round of groundwater sampling.

Response: This evaluates the impact to groundwater quality from suspended solids.

Comment # 4: Page 5-3, Section 5.4: It does not make much sense to not collect a subsurface sample at 3 – 5 ft bgs using DPT method because of budget constraints, if the sample is a critical sample. Recommend that any surface soil samples collected from 0.5 – 1.5 ft bgs be not analyzed for VOCs because most VOCs in the top 12 inches of surface soils will be lost to ambient air. The money saved could be used for the collection and analysis of the additional subsurface sample.

Response: This sample is not a critical location. Comment noted regarding the VOCs in surface soil.

Reviewer: Sam Bass, USACE - CX Geology

Comment # 1: Based on discussions with HTRW CX Counsel, the property transfer agreement(s) signed by NASA contains language that NASA accepted the property as is. As such, there appears to be no authority for USACE to be performing work at the Plum Brook site. Recommend you consult with District Counsel for further guidance on this issue before proceeding on this project. The following comments are offered to address technical issues in the document depending on the outcome of discussions with Counsel.

Response: Direction was received to proceed with investigation activities.

Comment # 2: Page 1-3, Section 1.1, last paragraph. What is the likelihood that the VOC and SVOC detections in the bedrock well are related to naturally-occurring hydrocarbons? If this is a possibility the plan should state this. Further, what are the possible sources for VOCs and SVOCs at the site if not from naturally-occurring substances? This has not been discussed other than generalizations about the processes used at the site.

Response: Naturally-occurring hydrocarbons are addressed on the following page.

Comment # 3: Page 3-4, Section 3.2.5. Decision statements for the site include determining physical characteristics of bedrock and whether bedrock ground water has been impacted by site contaminants. Therefore the vertical boundary of the study would include bedrock, not just the upper ten feet of soil. Similarly, the temporal boundaries should also include seasonal variations in bedrock ground water as well as shallow ground water. Please edit the plan accordingly.

Response: The statements about the upper 10 feet were in context to the soil investigation as stated in the first sentence. Obviously the study does not exclude the bedrock since monitoring wells will be installed in the bedrock.

Comment # 4: Page 3-4, Section 3.2.6; and Page 5-1, Section 5.3.1. One of the decision statements is to determine if ground water has been impacted by site contaminants. Making installation of monitoring wells dependent on whether conductive formation material is found could allow this objective to not be met. Recommend the project team evaluate the use of passive samplers, e.g., the HydraSleeve, for use in collecting ground water samples for semi-volatile and PCB analysis. Passive diffusion bag samplers are not recommended for semi-volatile analysis. Use of passive samplers will allow sample locations to be selected based on proximity to contaminant sources rather than the presence of conductive material.

Response: The comment implies that additional borings will be advanced at different locations until adequate yield is found. This investigation will place the wells at the proposed locations screened in the interval with the best yield based on professional judgment from soil cuttings.

Comment # 5: Page 3-4, Section 3.2.6. Please refer to EPA/600/R-96/055, Chapter 5. Decision Rules are intended to be structured as "if-then" statements. The discussion in Section 3.2.6 does not follow this paradigm. Also, the current discussion only addresses the placement of soil borings and whether wells will be installed or not. It does not address the other questions raised in the Problem Statement (determining contamination in soil, surface water, and sediment, i.e., what constitutes "contamination"?). Please modify the plan accordingly.

Response: An additional statement has been added to address the presence of contamination and additional actions that could be taken outside of the initial phase of work. However, the presence or absence of contamination in soil, surface water, sediment, or groundwater will not change the currently proposed activities.

Comment # 6: General comment. The presence of PCB contamination only near former storage tanks is puzzling, as PCBs are typically associated with electrical equipment. However, PCBs have also been used as pesticide extenders, dedusting agents, hydraulic fluids, and plasticizers in rubber. The presence of PCBs at the site may be the result of usage as intended (e.g., pesticide usage, breakdown of tires, etc.) rather than actual disposal. Recommend background samples be collected and analyzed for PCBs to determine the breadth of distribution. This sampling should also include areas around other buildings not involved in the acid production process or where transformers were known to not be present, to investigate the potential for application of PCBs in pesticide / herbicide mixtures.

Response: Comment noted, however background sampling or sampling at other sites is outside of the current scope of the project.

Comment # 7: General comment. The project team should collect surface water elevation data in the drainage ditches around the site in order to determine if ground water is discharging into the ditches or vice versa. It would also be instructive to know if the gradient reverses during high precipitation events, which indicates temporal data will also be required.

Response: Elevation data is collected for the surface water locations.

Comment # 8: Page 5-2, Section 5.3.1, first partial paragraph on page. Verify that the proposed 10- to 15-foot screen length for piezometers does not violate Ohio state guidance for well installations (which recommends a maximum 10-foot screen). Adjust piezometer screen length accordingly.

Response: Verified. The OEPA prefers this approach and these are not permanent wells.

Comment # 9: Page 5-2, Section 5.3.1, second paragraph on page. This paragraph states that new monitoring well locations will be based on water level contour maps from the 2004 ground water data summary, yet eight new piezometers are being installed to define "flow of shallow groundwater at the sites". Please correct the discrepancy. The implication is that piezometer data will be used to locate new monitoring wells. If data from the piezometers will not be used to select well locations they can be deleted from the drilling/sampling program. See previous comment on the use of the HydraSleeve for collection of water samples from wells in low-conductivity materials.

Response: The text has been revised to indicate that this reference is in relation to the bedrock well placement only.

Comment # 10: Page 5-2, Section 5.3.1, third paragraph on page. Please clarify how you will determine the "best water-yielding zone" in the overburden and bedrock. Will packer or geophysical tests be performed?

Response: The text has been revised to include yield determination.

Comment # 11: Page 5-2, Section 5.3.1, fourth paragraph on page. Please clarify how the final boring depth will be determined for bedrock wells, and whether the boring will need to be reamed upon completion of coring. Clarify that a casing will be set into the top of bedrock to prevent communication between the overburden and bedrock water-bearing zones. Provide details on the casing size and material, plus the composition of grout to be used to seal the casing into the boring.

Response: This information is addressed in the Site-Wide SAP.

Comment # 12: Page 5-3, Section 5.3.3. Additional field data to be gathered for ground water (not included on Table 3-1 of the QAPP) includes pH, temperature, dissolved oxygen, oxidation-reduction potential, and specific conductance.

Response: This information is addressed in the Site-Wide SAP.

Comment # 13: Page 5-4, Sections 5.4 and 5.5. The rationale for selection of analytical suites is unclear. There is nothing in the site history discussion that would indicate analysis for VOCs or SVOCs is required, particularly at sites that were primarily (solely?) used for storage of acid products. Also, the only contaminants found in previous sampling performed at the site (presumably with the same analytical suites) were nitroaromatics and PCBs. Unless there is specific information that indicates the potential use of VOCs and SVOCs at the site it appears analysis for these chemical classes could be deleted. Otherwise, please provide justification for all analytes selected for the project.

Response: The OEPA requires that USACE cover all the bases rather than presuming in order to satisfy public concern and to document adequate characterization has been performed.

Comment # 14: General comment. Many of these comments are the same comments made on the Sampling and Analysis Plan for Acid Areas 2 and 3. In the future, please ensure a quality control and lessons learned system is implemented to prevent or reduce repetition of common errors.

Response: The Final AA2&3 SAP served as the basis for the Draft AA1 SAP. All comments that were accepted during the AA2 & 3 response process were incorporated into the Final document and likewise carried over to the Draft AA1 SAP. Comments 4, 8, 10, 11, and 12 are repeat comments from the Acid Areas 2 and 3 SAP. These comments were addressed, however the reviewer may feel that the responses were not satisfactory. Comments 11 and 12 relate to information that is found in the Site-wide SAP, in the prior response and here also the reviewer is referred to the Site-wide SAP. Specific instructions were provided to Jacobs to reference the Site-wide SAP rather than repeat all of the material. Comment 10 was addressed in the AA2 &3 SAP but the focus apparently was on the

bedrock zones only – additional text has been added to address the over-burden. Comment 8 remains the same – the OEPA geologist prefers the current approach and the guidance referenced applies to permanent wells not temporary piezometers. Comment 4 remains the same – the OEPA preferred that sampling be conducted in a more traditional manner, although the suggestions are an excellent alternative. The reviewer should understand that not every suggestion will be accepted by the team and that this should not be interpreted as a repetition of common errors as suggested in the comment.

SUBJECT: Response to review comments for the Draft Sampling and Analysis Plan, Remedial Investigation, Part 1, at Acid Area 1, Former Plum Brook Ordnance Works (PBOW), Sandusky, OH, August 2005, Prepared by Jacobs Engineering Group, Inc., Contract Number DACW62-03-D-0004-0004

Reviewer: Julie Weatherington-Rice, TAPP

1.1 Site History and Contaminants

1. This is a good physical description of the probable historical activities at the site. We found it helpful in our understanding of activities.

Response: Comments Noted

1.2.2 Site Geology

2. Section 1.2.2 - Expect karstic characteristics in the Delaware Limestone under Acid Area 1 when the three bedrock wells are installed.

Response: Comment noted

3. If oil is encountered in the new bedrock drilling, could it be collected for fingerprinting analysis?

Response: NASA has been tasked with providing a fingerprint of the oil detected in bedrock wells at the PBOW facility.

1.2.3 Groundwater

4. See Figure 1 and Table 1 for more information on the dewatering rates at the Wagner Quarry. Note that Table 1 is in millions of gallons. Data for 2004, last year of information, shows a pumping rate of more than 1 million gallons per day.

Response: Comment noted.

5. Eric Dodrill, Erie Soil & Water Conservation District estimates that the Wagner Quarry is between 120 to 150 feet deep. They are quarrying all of the Delaware Limestone and most, if not all, of the Columbus Limestone. Eric is trying to arrange a preliminary visit to the quarry, in his roll with Erie SWCD.

Response: Comment noted

3.2.2 Problem Statement – Step 1

6. **This is a good description of the problem to be investigated for this project.**

Response: Comment Noted

3.2.1 Conceptual Site Model

7. **It has been our experience that railroad siding loading and unloading areas are often the location of spills. We recommend that the new soils sampling sites include significantly more sampling locations at the known and/or logical loading/unloading locations along the rail lines on either side of the site.**

Response: There are four logical materials transfer locations adjacent to four main storage facilities. Three of these locations were sampled during the 1998 site investigation; Sulphuric Acid Sales Storage (soil boring SB13), TNT Residual Acid Storage (soil boring SB02), and Mixed Storage (soil boring SB07). Sampling was not performed adjacent to the Oleum Storage facility. Soil boring SB-17 has been moved from the interior of the former Sulphuric Acid Sales Storage facility to the Oleum Storage facility to fill this data gap.

3.2.6 Decision Rules – Step 5

8. **This section indicates that the locations for new "soil borings will be biased toward former acid production facilities such as buildings, storage tanks, and disturbed areas". Please see our concern for Section 3.2.1.**

Response: See response to comment #7.

9.2 Sampling Apparatus and Field Instrumentation

9. **The term "Munsel chart" is more correctly titled the "Munsell Soil Color Charts". Please correct here and anywhere else in the text that this reference is made.**

Response: The suggested change has been incorporated.

Figure 1-2 Acid Area 1 Contaminant Distribution

10. **The blocks of contaminants are very difficult to read at this scale. It would be helpful if the boxes were bigger, a bigger figure (such as 11x17) was included, and/or there was a table right behind the figure that listed each analysis so that they could easily be checked against the graphic.**

Response: The figure has been enlarged as requested.

Figure 3-1 Acid Area 1 Soil Boring Locations

11. Again, there appears to be limited information gathered along the loading/offloading locations on the rail lines where spills would have typically occurred. Please add more borings at known and/or interpreted rail transport locations to identify possible spill sites.

Response: See response to comment #7

Figure 5-1 Acid Area 1 Groundwater Sampling Locations

12. The depths of the new bedrock ground water monitoring wells need to be determined, in part, by the lowest static water levels at AA1-BEDGW-001 and MNTA-BEDGW-001 for late summer and fall of 1999 if there are readings for that period for these wells. This was the last serious drought year for this area. In addition, the pumping cone from the Wagner Quarry must also be considered in determining the target depth for the three new wells. If they are finished too high, they will be dry part or all of the time.

Response: Water levels in the Delaware Limestone at AA1 range from 20' – 30' below ground surface. The bottom of the well screen will be installed at minimum depth of 50' for all bedrock monitoring wells. The text has been revised to include this additional specification.

QAPP

FINAL SITE-SPECIFIC QUALITY ASSURANCE PROJECT PLAN

REMEDIAL INVESTIGATION, PART 1, AT ACID AREA 1 FORMER PLUM BROOK ORDNANCE WORKS SANDUSKY, OHIO

Prepared for:

DEPARTMENT OF THE ARMY
NASHVILLE DISTRICT, CORPS OF ENGINEERS
NASHVILLE, TENNESSEE
CONTRACT DACW62-03-D-0004-0007

Prepared by:

JACOBS ENGINEERING GROUP, INC.
125 BROADWAY
OAK RIDGE, TN 37830

April 2007

COMPLETION OF INDEPENDENT TECHNICAL REVIEW

Jacobs Engineering Group, Inc. has completed the Final Site-Specific Quality Assurance Project Plan for the Acid Area 1 Remedial Investigation Part 1: Site Characterization at the Former Plum Brook Ordnance Works, Sandusky, Ohio. Notice is hereby given that an independent technical review has been conducted that is appropriate to the level of risk and complexity inherent in the project, as defined in the Quality Control Plan. During the independent technical review, compliance with established policy principles and procedures, utilizing justified and valid assumptions, was verified. This included review of assumptions; methods, procedures, and material used in analyses; alternatives evaluated; the appropriateness of data used and level of data obtained; and reasonableness of the results, including whether the product meets the customer's needs consistent with law and existing Corps policy.

(Signature)	Geologist (Discipline)	4/12/07 (Date)

Independent Technical Review Team Leader and Team Members

(Signature)	(Discipline)	(Date)

Independent Technical Review Team Leader and Team Members

(Signature)	(Discipline)	(Date)

Independent Technical Review Team Leader and Team Members

Al Hardesty (Signature)	Geologist (Discipline)	4/12/07 (Date)

Jacobs QAPP Addendum Author

CERTIFICATION OF INDEPENDENT TECHNICAL REVIEW

Responses to comments from the PBOW Team review are provided as appendices to the document and changes have been incorporated as appropriate.

All concerns resulting from independent technical review of the project have been considered.

Al Hardesty — (Signature)

4/12/07 — (Date)

(Project Manager)

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LIST OF ACRONYMS AND ABBREVIATIONS

CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
CQAR	Chemical Quality Assurance Report
DoD	Department of Defence
ELAB	Elab of Tennessee, LLC
EPA	U.S. Environmental Protection Agency
ft	foot
HTRW-CX	Hazardous, Toxic, Radioactive Waste Center of Expertise
IDW	investigation-derived wastes
MDL	method detection limit
MRL	method reporting limit
MS/MSD	matrix spike / matrix spike duplicate
NFG	USEPA National Functional Guidelines for Data Review
PCB	polychlorinated biphenyl
PM	Project Manager
PRG	preliminary remediation goal
QAPP	Quality Assurance Project Plan
QA	quality assurance
QC	quality control
QSM	Department of Defense "Quality Systems Manual for Environmental Laboratories," Version 3, January 2006
RBC	risk-based criteria
RCRA	Resource Conservation and Recovery Act
SAP	Sampling and Analysis Plan
SSFSP	Site-Specific Field Sampling Plan
SSQAPP	Site-Specific Quality Assurance Project Plan
SOP	standard operating procedure
SVOC	semi-volatile organic compound
SVTU	Severn Trent Laboratories, University Park, Illinois
SWSAP	Site-Wide Sampling and Analysis Plan
TAL	Target Analyte List
TCL	Target Compound List
TCLP	Toxicity Characteristic Leaching Procedure
T&D	transportation and disposal
USACE	U.S. Army Corps of Engineers
VOC	volatile organic compound

1.0 PROJECT LABORATORY ORGANIZATION AND RESPONSIBILITIES

This Site-Specific Quality Assurance Project Plan (SSQAPP) combined with the Site-Specific Field Sampling Plan (SSFSP) form the Sampling and Analysis Plan (SAP) for the Remedial Investigation (RI), Part 1, at Acid Area 1. This SSQAPP is an addendum to the Site-Wide Quality Assurance Plan (SWQAPP) (Jacobs 2004a) prepared as part of the Former Plum Brook Ordnance Works Site-Wide Sampling and Analysis Plan (SWSAP) (Jacobs 2004a and Jacobs 2004b). The SWQAPP provides the overall requirements for sample collection and analyses to ensure that the data collected is complete and of suitable quality for the decision-making purposes associated with the RI at Acid Area 1 located at the former Plum Brook Ordnance Works in Sandusky, Ohio. The work is being performed by Jacobs for the United States Army Corps of Engineers (USACE), Nashville District. Jacobs has prepared this QAPP under Contract No. DACW62-03-D-0004, Task Order Number 0007.

The Department of Defense "Quality Systems Manual for Environmental Laboratories," Version 3, January 2006 (DOD QSM), provided the format and standard text used in the preparation of this QAPP. The United States Environmental Protection Agency (EPA), *Instructions on the Preparation of a Superfund Division Quality Assurance Project Plan* EPA, 2000, which is based on *EPA Requirements for Quality Assurance Project Plans, Interim Final* EPA QA/R-5, 1999, was reviewed and applicable requirements addressed in this document.

Empircal Laboratories (ELAB) will provide analytical support as the primary laboratory. They will perform all primary analyses at their Nashville, Tennessee facility. Severn Trent Laboratories of University Park, Illinois (SVTU) will provide analytical support as the Quality Assurance (QA) laboratory. They will perform all QA analyses, at their University Park, IL facility.

ELAB and SVTU meet the requirements of the Department of Defense Quality Systems Manual verification process and have current letters of verification from the Department of the Navy. The laboratories will be required to maintain this validation for all applicable methods throughout the life of the project. This validation confirms their ability to produce reliable and defensible data. Approval of this plan constitutes USACE approval of the selected laboratories to provide the required project-specific analyses. The laboratory verification letters are contained in Appendix A.

The laboratory contacts are as follows:

Marcia McGinnity
Empirical Laboratories
227 French Landing Suite 550
Nashville, TN 37228
Phone: 615-345-1115
Fax: 615-846-5426

Linda Mackley
Severn Trent Laboratories, Inc.
2417 Bond Street
University Park, IL 60466
Phone: 708-534-5200
Fax: 708-534-5211

1.1 ANALYTICAL LABORATORY PROJECT MANAGER

The ELAB and SVTU Project Mangers, Marcia McGinnity and Linda Mackley, respectively, are designated to act as single points of contact at the primary and QA laboratories, respectively, and coordinate project details with the Jacobs' Project Chemist and Program Manager. Section 1.1 of the SWQAPP (Jacobs 2004a) provides greater detail on the analytical laboratory Project Managers' responsibilities.

1.2 ANALYTICAL LABORATORY QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) DIRECTOR

Randy Ward and Therese Preston are the QA/QC Directors at ELAB and SVTU, respectively, and are identified as such on the laboratory organizational charts in Appendix B of this QAPP. Section 1.2 of the SWQAPP (Jacobs 2004a) provides greater detail on the analytical QA/QC Directors' responsibilities.

1.3 ANALYTICAL LABORATORY TECHNICAL MANAGERS

Rick Davis and Mike Healy are the analytical subcontractor Technical Managers for ELAB and SVTU, respectively. They are identified as such on the laboratory organizational charts in Appendix B of this QAPP. Section 1.3 of the SWQAPP (Jacobs 2004a) provides greater detail on the analytical laboratory Technical Managers' responsibilities.

2.0 DATA ASSESSMENT ORGANIZATION AND RESPONSIBILITIES

Refer to Section 2.0 of the SWQAPP (Jacobs 2004a).

2.1 PRIMARY SAMPLE DATA ASSESSMENT

Section 2.1 of the SWQAPP (Jacobs 2004a) presents the three-step data review process. Third-party data validation is not required for this investigation; however this data set will be validated following protocol set forth in the QSM and qualification flags will be applied by Jacobs' personnel who are independent of the project. 100% of the primary sample data will be evaluated per the procedure in Section 8.2 of the SWQAPP (Jacobs 2004a) since the intended data use is for estimating risk at the site. Lonnie Fallin, the Jacobs Project Chemist, will be responsible for completing the verification/validation of the primary sample data. Mr. Fallin reports directly to the Jacobs Program Manager, Al Hardesty.

2.2 QA SAMPLE DATA ASSESSMENT

The QA sample data will be validated like the primary data and compared to the associated primary sample results, and a Chemical Quality Assurance Report (CQAR) will be issued comparing and evaluating the primary and QA sample results. The data assessment and CQAR will be prepared per the requirements of USACE-HTRX-CX, EM-200-1-6 *Chemical Quality Assurance for HTRW Projects,* October 1997.

3.0 DATA QUALITY OBJECTIVES

Section 3.0 of the SSFSP (Jacobs 2004c) provides the investigation objectives and data needs for the RI at the Acid Areas.

3.1 DATA USE BACKGROUND

The specific data needs for Acid Area 1 have been developed based on the existing Site Investigation (SI) performed by IT Corporation (IT) in 1998. The following sections describe the types of samples planned for this remedial investigation and the types of analyses and data required to support the project data needs.

3.1.1 Soil Remedial Investigations

Soil samples will be collected to conduct further investigation of process facilities at Acid Area 1 not characterized during the 1998 SI. Sample locations and rationale are presented in Section 3.2.8 of the Site-Specific FSP. Forty-five samples collected from direct push borings (Subject to field conditions, it is anticipated that samples will be collected from the 0.5 to 1.5 ft below ground surface and at 3 to 5 ft below ground surface at each borehole).The soil samples are considered critical samples and will require methods capable of producing definitive data and a full data package as specified in Section 7.2 of the SWQAPP (Jacobs 2004a). The soil samples will be analyzed using USEPA SW-846 methodology and the USEPA Contract Laboratory Program (CLP) Target Analyte List/Target Compound List (TAL/TCL). Table 3-1 of this QAPP provides the number of field samples, QA samples, and QC samples associated with this effort. Table 3-2 provides the method holding times, containers, and preservation for the applicable methods. The required chemical parameters for the soil samples for each method are listed in Tables 3-3 through 3-13. The soil RI samples will be analyzed using the following analytical methods:

- TCL VOCs (SW-846 5035/8260B)
- TCL SVOCs (SW-846 3540C/8270C)
- TCL PCBs (SW-846 3540C/8082)
- Nitroaromatics (SW-846 8330)
- TAL Metals (SW-846 3050B/6010C/7471A series)

3.1.2 Surface Water And Sediment Sampling

Fifteen sets of collocated surface water and sediment samples will be collected in the vicinity Acid Area 1. The surface water and sediment samples are considered critical samples and require methods capable of producing definitive data and a full data package as specified in Section 7.2 of the SWQAPP (Jacobs 2004a). The surface water and sediment samples will be analyzed using USEPA SW-846 methodology and the USEPA CLP TAL/TCL, which includes all compounds including nitroaromatics. Table 3-1 of this QAPP provides the number of field samples, QA samples, and QC samples associated with this effort. Table 3-2 provides the method holding times, containers, and preservation for the applicable methods. The required chemical parameters for the surface water and sediment samples for each method are provided in Tables 3-3 through 3-13. The surface water and sediment remedial investigation samples will be analyzed by the following methods:

- TCL VOCs (SW-846 8260B with 5035 for sediments, and 5030 for surface waters)
- TCL SVOCs (SW-846 8270C with 3540C for sediments and 3510C for surface waters)
- PCBs (SW-846 8082 with 3540C for sediments and 3510C for surface waters)
- Nitroaromatics (SW-846 8330)
- TAL Metals (SW-846 3050B/6010C/7471A for sediments, and SW-846 3005A/6010C/7470A for surface waters)

3.1.3 Groundwater Monitoring Well Sampling

Ten groundwater monitoring wells will be sampled quarterly for at least two rounds to determine impacts of the Acid Area 1 process facilities on the groundwater. Four existing wells and six new wells at Acid Area 1 will be sampled. The purpose of the groundwater monitoring samples is to determine impacts to the shallow and bedrock groundwater from the process facilities at the Acid Areas, and to collect data of appropriate quality to support a risk assessment and feasibility study. The groundwater monitoring samples are considered critical samples and require methods capable of producing definitive data and a full data package as specified in Section 7.2 of the SWQAPP (Jacobs 2004a). The samples will be analyzed using USEPA SW-846 methodology and the USEPA CLP TAL/TCL. Table 3-1 of this QAPP provides the number of field samples, QA samples, and QC samples associated with this effort. Table 3-2 provides the method holding times, containers, and preservation for the applicable methods. The required chemical parameters for the groundwater monitoring samples for each method are provided in Tables 3-3 through 3-13. Samples for dissolved metals will be collected for the initial round of groundwater monitoring samples only. The samples for dissolved metals will be filtered in the field using a 45-micron in-line filter prior to sample collection. The groundwater monitoring samples will be analyzed by the following methods:

- TCL VOCs (SW-846 5030/8260B)
- TCL SVOCs (SW-846 3510C/8270C)
- PCBs (SW-846 3510C/8082)
- Nitroaromatics (SW-846 8330)
- TAL Metals (SW-846 3005A/6010C/7470A series) (total and dissolved for initial round of groundwater samples)
- Water Quality Parameters (see Table 3-1 of this QAPP)

3.1.4 Investigation Derived Waste Sampling

Investigative derived waste (IDW) samples will be collected from 55-gallon drums of waste containerized by waste type and stored at the site. A total of eight IDW samples are expected to be collected. The samples will be analyzed by the transportation and disposal subcontractor (T&D), Integrated Solutions and Services, Inc. or their analytical

subcontractor. The IDW sample analyses will meet all applicable Resource Conservation and Recovery Act (RCRA) requirements and the requirements of the party accepting the material for final disposition. The IDW samples are considered noncritical samples. Integrated Solutions and Services will analyze the samples using SW-846 Toxicity Characteristic Leaching Procedure (TCLP) methods. The standard RCRA TCLP contaminant list, and the standard RCRA TCLP maximum concentration of contaminants will serve as the sensitivity requirement for the TCLP analyses. Table 3-1 of this QAPP provides the number of field samples, QA samples, and QC samples associated with this effort. Table 3-2 provides the method holding times, containers, and preservation for the applicable methods. A standard Level II data package containing sample results and a case narrative as specified in Section 7.2 of the SWQAPP (Jacobs 2004a) is required for the IDW sample analyses. The IDW samples will be analyzed by the following methods:

- TCLP VOCs (SW-846 1311/5030/8260B)
- TCLP SVOCs (SW-846 1311/3510C/8270C)
- TCLP Metals (SW-846 1311/3005A/6010C/7470A series)
- Reactivity, Corrosivity, and Ignitability per SW-846 Chapter 7

Jacobs subcontract with the T&D contractor will be structured such that it is the responsibility of the T&D subcontractor to arrange for analytical services and ensure that the analytical strategy is appropriate and acceptable to the party accepting the material for final disposition.

3.2 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

Refer to Section 3.2 of the SWQAPP (Jacobs 2004a).

3.2.1 Sensitivity

The sensitivity requirements for analytes are based on the Region IX Preliminary Remediation Goals (PRGs) for this project. This is a change from the SWQAPP (Jacobs 2004a) that based the sensitivity requirements on the Region III risk based screening criteria. The change to the Region IX PRGs was based on comments from the regulatory agencies for the RI performed at Reservoir Number 2 Burning Ground at Plum Brook Ordnance Works. The Region IX PRGs, laboratory method reporting limits (MRLs), and method detection limits (MDLs) are provided in Tables 3-3 through 3-13 of this QAPP. These tables provide the sensitivity requirements (project objectives) for each sample matrix and parameter of interest for the analytical methods for the RI activities associated with the Acid Areas, and compares the sensitivity requirements to the actual analytical subcontractors' MRLs and MDLs for each chemical parameter of interest.

Analytical methods have been selected to meet the project data quality objectives for the parameters in each matrix using SW-846 methods, some laboratory MRLs and MDLs are above the project screening objectives. The values where the laboratory MDLs and/or MRLs exceed the Region IX PRGs are shaded in Tables 3-3 through 3-13. These outliers are due to the fact that the sensitivity goals were developed in accordance with risk-based calculations without regard to the constraints of current analytical technology. The SW-846 methods capable of achieving the project data quality objectives have been selected to meet as many of the PRGs as possible. Compounds that do not meet the sensitivity requirements will be addressed in the uncertainty analysis of the risk assessment.

3.2.2 Precision

Section 3.2.2 of the SW QAPP (Jacobs 2004a) provides the field and laboratory precision requirements. Table 3-1 of this QAPP provides the total number environmental samples, field duplicates, and other QA/QC samples planned for the Acid Areas. Table 3-14 of this QAPP provides the laboratory precision and accuracy goals. All laboratory precision goals identified in the SWQAPP (Jacobs 2004a) and this QAPP are applicable.

3.2.3 Accuracy

Section 3.2.3 of the SWQAPP (Jacobs 2004a) provides the field and laboratory accuracy requirements. Table 3-14 of this QAPP provides the laboratory precision and accuracy goals. All laboratory accuracy goals identified in the SWQAPP (Jacobs 2004a) and this QAPP are applicable.

3.2.4 Completeness

Section 3.2.4 of the SWQAPP (Jacobs 2004a) provides the field and laboratory completeness requirements that are applicable to this RI.

3.2.5 Representativeness

Section 3.2.5 of the SWQAPP (Jacobs 2004a) provides the field and laboratory representativeness requirements. These requirements are integral to this RI.

3.2.6 Comparability

Section 3.2.6 of the SWQAPP (Jacobs 2004a) provides the field and laboratory comparability requirements that are applicable to this RI.

4.0 SAMPLE RECEIPT, CUSTODY, AND HOLDING TIME REQUIREMENTS

Section 4.0 of the SWQAPP (Jacobs 2004a) provides the sample receipt, custody, and holding time requirements. Table 3-2 of this QAPP provides the holding time requirements for each analytical method. Appendix C of this QAPP provides the subcontract laboratory SOPs for sample receipt, handling, and custody.

5.0 ANALYTICAL PROCEDURES

The analytical subcontractors selected to support this program will implement method-specific laboratory SOPs for sample preparation, cleanup and analysis for each method required by the this QAPP. These laboratory SOPs are based on methods from SW-846 Final Update III, Revision 4 (December 1996). The specific laboratory SOPs required to support the investigation at the Acid Areas are included in Appendix C of this QAPP. Table 3-1 of this QAPP provides the number of samples and required analyses for each sample type.

5.1 LIST OF METHODS, TARGET COMPOUNDS AND LABORATORY QUANTITATION LIMITS

Complete listings of chemical parameters of concern by analytical method, the subcontract analytical laboratories' MDLs and MRLs, and the Region IX Preliminary Remediation Goals for each parameter of concern are provided in Tables 3-3 through 3-13 of this QAPP. MDLs shown in these tables are experimentally determined using the method found in 40 Code of Federal Regulations (CFR), Part 136 for each instrument at each of the subcontract analytical laboratories. The MRLs are based on the lowest calibration standard used in initial calibration for each method.

5.2 LABORATORY INSTRUMENT PREVENTATIVE MAINTENANCE

Section 5.2 of the SWQAPP (Jacobs 2004a) provides a discussion on the required laboratory instrument preventative maintenance.

5.3 LABORATORY CALIBRATION PROCEDURES AND FREQUENCY

Section 5.3 of the SWQAPP (Jacobs 2004a) provides a discussion on the laboratory instrument calibration procedures and frequency.

5.4 QUALITY CONTROL REQUIREMENTS

Section 5.4 of the SWQAPP (Jacobs 2004a) provides the requirements of field, analytical, and batch quality control. Table 3-1 of this QAPP provides a summary of the types and frequency of collection for QA/QC samples planned in support of the RI at the Acid Areas.

Acceptance criteria and/or target ranges for QC samples are provided in Table 3-14 of this QAPP for each of the required analytical methods. The criteria provided in Table 3-14 is based on Appendix B, *Final Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 3* (DoD; January 2006). For methods not included in this document, the internal laboratory limits and control ranges will be used.

5.5 PERFORMANCE AND SYSTEM AUDITS

Section 5.5 of the SWQAPP (Jacobs 2004a) provides a discussion on the requirements and types of audits that may be performed in conjunction with this RI.

5.6 NONCONFORMANCES AND CORRECTIVE ACTIONS

Section 5.6 of the SWQAPP (Jacobs 2004a) provides the requirements of the nonconformance and corrective action system that the program and this RI will follow.

5.7 QUALITY ASSURANCE REPORTS TO MANAGEMENT

Section 5.7 of the SWQAPP (Jacobs 2004a) provides a discussion on the quality reporting system for the program and this RI.

6.0 DATA REDUCTION/CALCULATION OF DATA QUALITY INDICATORS

Section 6.0 of the SWQAPP (Jacobs 2004a) provides the field and laboratory data reduction procedures, and the data usability reconciliation process. Tables 3-3 through 3-13 provide the sensitivity requirements and the laboratory MRLs and MDLs for each chemical parameter of concern for the RI at the Acid Areas. The sensitivity requirements for this project are the Region IX PRGs. This is a change from the Region III risk based screening criteria required by the SWQAPP (Jacobs 2004a).

7.0 DATA REPORTING

Section 7.0 of the SWQAPP (Jacobs 2004a) provides the field and laboratory data reporting formats, the electronic data deliverable format, and the data retention and sample archival and disposal requirement. The analytical turnaround time for the data collected in support of the RI at Acid Area 1 will be 30 calendar days from receipt of the samples.

8.0 DATA MANAGEMENT

Section 8.0 of the SWQAPP (Jacobs 2004a) provides the data review, verification, and validation procedures. Data validation/verification for this project will be performed in accordance with the procedures detailed in Section 8.2 of the SWQAPP (Jacobs 2004a).

9.0 REFERENCES

Department of Defense (DoD), January 2006. *Final Quality Systems Manual for Environmental Laboratories, Final Version 3.*

EPA, January 2000. Final *Data Quality Objectives Process for Hazardous Waste Site Investigations*, QA/G-4HW, 2000, Office of Environmental Information, Washington, DC.

EPA, March 2001. *EPA Requirements for Quality Assurance Project Plans (QA/R-5).* EPA/240/B-01/003.

EPA, December 1996. *Test Methods for Evaluating Solid Waste, Final Update III*, SW-846.

EPA, October 1999. *Contract Laboratory Program National Functional Guidelines for Organic Data Review.* EPA 540/R-99/008, OSWER 9240.1-05A-P.

EPA, February 1994. *Contract Laboratory Program National Functional Guidelines for Inorganic Data Review.* EPA 540/R-94/013, OSWER 9240.1-05-01.

Jacobs, May 2004a. *Final Site-Wide Quality Assurance Plan, Former Plumbrook Ordnance Works Sandusky, Ohio.*

Jacobs, May 2004b. *Final Site-Wide Field Sampling Plan, Former Plumbrook Ordnance Works Sandusky, Ohio.*

USACE-HTRX-CX, September 1994. *Requirements for the Preparation of Sampling and Analysis Plans.* EM-200-1-3.

USACE-HTRX-CX, October 1997. *Chemical Quality Assurance for HTRX Projects.* EM-200-1-6.

QAPP Tables

TABLES

TABLE 3-1

PLUMBROOK ORDNANCE ACID AREA 1
SAMPLE SUMMARY

SAMPLE DESCRIPTION/ LOCATIONS	MATRIX	SAMPLE TYPE	ANALYTICAL PARAMETERS/ METHODS	NUMBER AND TYPE OF FIELD SAMPLES				
				Primary/ QA	Duplicate	Trip Blank	MS/ MSD	Equipment Rinsate
Acid Area 1 Soil Sampling	Soil	DPT Boring	TCL VOCs (5035/8260B) TCL SVOCs (3540C/8270C) PCBs (3540C/8082) Nitroaromatics (8330) TAL Metals (3050B/6010B/ 7471A)	45/5	5	0	4 (2 pair)	5
Acid Area 1 Sediment Sampling	Sediment	Grab	TCL VOCs (5035/8260B) TCL SVOCs (3540C/8270C) PCBs (3540C/8082) Nitroaromatics (8330) TAL Metals (3050B/6010B/ 7471A)	15/2	2	0	1 (1 pair)	2
Acid Area 1 Surface Water Sampling	Surface Water	Grab	TCL VOCs (5030/8260B) TCL SVOCs (3510C/8270C) PCBs (3510C/8082) Nitroaromatics (8330) TAL Metals (3005A/6010/ 7470A)	15/2	2	2	1 (1 pair)	2
Groundwater monitoring well samples	Ground-water	Grab	TCL VOCs (5030/8260B) TCL SVOCs (3510C/8270C) PCBs (3510C/8082) Nitroaromatics (8330) TAL Metals (3005A/6010/ 7470A) Turbidity	20/4	4	4	4 (2 pair)	2

			(EPA180.1) Alkalinity (EPA 310.1) Hardness (EPA 130.2) TOC (SW-846 9060) TDS (EPA 160.1) TSS (EPA 160.2) Chloride (EPA 300) Nitrate (EPA 300) Sulfate (EPA 300) Cyanide (SW-846 9010A/9012) Dissolved TAL Metals (3005A/6010/ 7470A)	13/2	2	0	2 (1 pair)	1
IDW samples	Waste	Grab	TCLP VOC (1311/5030/ 8260B) TCLP SVOC (1311/3510C/ 8270C) TCLP Metals (1311/5030/ 6010B) (1311/7470A) Reactivity (SW-846 Ch. 7.3.3.2/7.3.4.2) Corrosivity (9045C) Ignitability (1010/1030)	3/0	0	0	0	0

TABLE 3-2
PLUMBROOK ORDNANCE ACID AREAS
TEST METHODS, CONTAINERS, PRESERVATIVES, AND HOLDING TIMES

Parameter	EPA Method [1]	Required Containers [2, 3]	Required Preservative	Maximum Holding Times (measured from sample collection)	
				To Extraction	To Analysis
Soils/ Sediments:					
VOCs	5035/8260B	3 x 5-gram EnCore samplers or equivalent	Cooled to 4±2°C	48 Hours to Preservation	14 Days
SVOCs	3540C/8270 C	8 oz Glass	Cooled to 4±2°C	14 Days	40 Days
PCBs	3540C/8082	8 oz Glass	Cooled to 4±2°C	14 Days	40 Days
Nitroaromatics	8330	8 oz Glass	Cooled to 4±2°C	14 Days	40 Days
Metals	3050B/6010 C	8 oz Glass	N/A	N/A	180 Days
	7471A (Hg by CVAA)	Included above	N/A	N/A	28 Days
Solid IDW Samples					
TCLP-VOC	1311/5030/ 8260B	4 oz Glass or 25 gram encore sleeve	Cooled to 4±2°C	14 Days to TCLP extraction	14 Days from TCLP to analysis
TCLP-SVOC	1311/3510C/ 8270C	8 oz Glass	Cooled to 4±2°C	14 Days to TCLP extraction 7 Days from TCLP extraction to preparative extraction	40 Days
TCLP Metals	1311/3005A/ 6010B	8 oz Glass	Cooled to 4±2°C	180 Days to TCLP extraction	180 Days from TCLP to analysis
TCLP Mercury	1311/7470A	Included with above TCLP Metals aliquot	Cooled to 4±2°C	28 Days to TCLP extraction	28 Days from TCLP to analysis
Ignitability (open-cup)	1010/1030	8 oz Glass	Cooled to 4±2°C	N/A	Analyze ASAP
Corrosivity	9045C	Included with 1010/1030	Cooled to 4±2°C	N/A	Analyze ASAP
Reactivity (Cyanide and Sulfide)	SW-846 Chapter 7.3.3.2 & 7.3.4.2	Included with 1010/1030	Cooled to 4±2°C	N/A	Analyze ASAP

TABLE 3-2 (Continued)

Parameter	EPA Method [1]	Required Containers [2, 3]	Required Preservative	Maximum Holding Times (measured from sample collection)	
				To Extraction	To Analysis
WATERS:					
VOCs	5030/8260B	3 x 40 ml Glass Vials	PH <2 HCL Cooled to 4±2°C	N/A	14 Days (if preserved, 7 days if unpreserved)
SVOCs	3510C/8270 C	1000 ml Amber Glass	Cooled to 4±2°C	7 Days	40 Days
PCBs	3510C/8082	1000 ml Amber Glass	Cooled to 4±2°C	7 Days	40 Days
Nitroaromatics	8330	1000 ml Amber Glass	Cooled to 4±2°C	7 Days	40 Days
Metals	3005A/6010 C	500 ml Poly	PH <2 HNO3	N/A	180 Days
	7470A (Hg by CVAA)	Included above	PH <2 HNO3	N/A	28 Days
Turbidity	EPA 180.1	125 ml Poly	Cooled to 4±2°C	N/A	48 Hours
Alkalinity	EPA 310.1	250 ml Poly	Cooled to 4±2°C	N/A	14 Days
Hardness	EPA 130.2	125 ml Poly	PH <2 HNO3 Cooled to 4±2°C	N/A	180 Days
Total Organic Carbon	9060	125 ml Poly	PH <2 HCL Cooled to 4±2°C	N/A	28 Days
Total Dissolved Solids	EPA160.1	500 ml Poly	Cooled to 4±2°C	N/A	7 Days
Total Suspended Solids	EPA 160.2	500 ml Poly	Cooled to 4±2°C	N/A	7 Days
Chloride	EPA 300	250 ml Poly	None	N/A	28 Days
Nitrate	EPA 300	250 ml Poly	Cooled to 4±2°C	N/A	48 Hours
Sulfate	EPA 300	250 ml Poly	Cooled to 4±2°C	N/A	28 Days
Cyanide	9010A/9012	250 ml Poly	NaOH pH>12, Cooled to 4±2°C	N/A	14 Days

TABLE 3-2 (Continued)

Parameter	EPA Method [1]	Required Containers [2,3]	Required Preservative	Maximum Holding Times (measured from sample collection)	
				To Extraction	To Analysis
Liquid IDW Samples:					
TCLP-VOC	1311/5030/ 8260B	3 x 40 ml Glass Vials	Cooled to 4±2°C	14 Days to TCLP extraction	14 Days from TCLP to analysis
TCLP-SVOC	1311/3510C/ 8270C	1000 ml Glass	Cooled to 4±2°C	14 Days to TCLP extraction 7 Days from TCLP extraction to preparative extraction	40 Days
TCLP Metals	1311/3005A/ 6010B	2 x 1000 ml Poly	Cooled to 4±2°C	180 Days to TCLP extraction	180 Days from TCLP to analysis
TCLP Mercury	1311/7470A	Included with above TCLP Metals aliquot	Cooled to 4±2°C	28 Days to TCLP extraction	28 Days from TCLP to analysis
Ignitability (open-cup)	1010/1030	1000 ml Poly	Cooled to 4±2°C	N/A	Analyze ASAP
Corrosivity	9040B	Included with 1010/1030	Cooled to 4±2°C	N/A	Analyze ASAP
Reactivity (Cyanide and Sulfide)	SW-846 Chapter 7.3.3.2 & 7.3.4.2	Included with 1010/1030	Cooled to 4±2°C	N/A	Analyze ASAP

[1] USEPA OSWER SW-846, Final Update III, Revision 4 methods.
[2] All soil containers will have Teflon-lined caps or septa. HDPE = high density polyethylene.
[3] For MS/MSD samples, additional sample volumes will be required as follows:
- VOCs: 1 times the sample volume
- SVOCs/pesticides/PCBs: 2 times the sample volume
- Metals: no additional sample volume required.

TABLE 3-3
Soil and Sediment Volatile Target Compound List
5035/8260B

Analyte	Region 9 PRG (ug/kg)	Primary Lab MRL (ug/kg)	Primary Lab MDL (ug/kg)	QA Lab MRL (ug/kg)	QA Lab MDL (ug/kg)
Dichlorodifluoromethane	9.4E+04	10	.31	2	0.45
Chloromethane	1.2E+03	10	.36	2	0.41
Bromomethane	3.9E+03	10	1.05	2	0.97
Vinyl chloride	7.9E+01	10	.28	0.5	0.25
Chloroethane	3.0E+03	10	.23	2	0.38
Trichlorofluoromethane	3.9E+05	10	.26	2	0.34
1,1,2-Trichloro-1,2,2-trifluoroethane	5.6E+06	10	.21	NA	NA
Methylene chloride	9.1E+03	10	.32	2	0.59
Acetone	1.6E+06	50	2.05	4	1.23
Carbon disulfide	3.6E+05	5	.40	2	0.18
Methyl acetate	2.2E+07	5	.57	NA	NA
1,1-Dichloroethene	1.2E+05	5	.30	1	0.27
1,1-Dichloroethane	5.1E+05	5	.21	1	0.20
cis-1,2-Dichloroethene	4.3E+04	5	.41	1	0.28
trans-1,2-Dichloroethene	6.9E+04	5	.26	1	0.20
Methyl tert-butyl ether	6.2E+04	5	.26	2	0.24
Chloroform	3.6E+03	5	.19	1	0.20
1,2-Dichloroethane	2.8E+02	5	.22	1	0.25
2-Butanone	7.3E+06	50	2.41	2	1.11
Bromochloromethane		10	.27	2	0.32
1,1,1-Trichloroethane	1.2E+06	5	.20	1	0.16
Cyclohexane	1.4E+05	5	.21	NA	NA
Carbon tetrachloride	2.5E+02	5	.19	1	0.59
Bromodichloromethane	8.2E+02	5	.27	2	0.17
1,2-Dichloropropane	3.4E+02	5	.20	1	0.26
cis-1,3-Dichloropropene	7.8E+02	5	.28	1	0.19
Trichloroethene	5.3E+01	5	.17	0.5	0.22
Methylcyclohexane	2.6E+06	5	.19	NA	NA
Dibromochloromethane	1.1E+03	5	.19	2	0.26
1,1,2-Trichloroethane	7.3E+02	5	.12	1	0.33
Benzene	6.0E+02	5	.20	0.5	0.088
trans-1,3-Dichloropropene	7.8E+02	5	.22	1	0.37
Bromoform	6.2E+04	5	.23	2	0.35
Isopropylbenzene	5.7E+05	5	.21	2	0.41
4-Methyl-2-pentanone	7.9E+05	25	.52	2	1.27
2-Hexanone		25	.63	2	1.23
Tetrachloroethene	1.5E+03	5	.23	1	0.39
1,2-Dibromoethane	6.9E+00	5	.27	2	1.33

TABLE 3-3 (continued)

Analyte	Region 9 PRG (ug/kg)	Primary Lab MRL (ug/kg)	Primary Lab MDL (ug/kg)	QA Lab MRL (ug/kg)	QA Lab MDL (ug/kg)
Toluene	5.2E+05	5	.23	0.5	0.12
1,1,2,2-Tetrachloroethane	4.1E+02	5	.20	1	0.27
Chlorobenzene	1.5E+05	5	.21	1	0.24
Ethylbenzene	8.9E+03	5	.23	1	0.17
Styrene	1.7E+06	5	.21	1	0.32
Xylenes (total)	2.7E+05	5	.66	1	0.29
1,2-Dibromo-3-chloropropane	4.5E+02	10	.25	2	0.70
1,3-Dichlorobenzene	1.6E+04	5	.17	2	0.55
1,4-Dichlorobenzene	3.4E+03	5	.24	2	0.47
1,2-Dichlorobenzene	3.7E+05	5	.17	2	0.51
1,2,3-Trichlorobenzene		5	.25	2	0.98
1,2,4-Trichlorobenzene	6.5E+05	5	.25	2	1.29

TABLE 3-4
Soil and Sediment Semi-Volatile Target Compound List
3540C/8270C

Analyte	Region 9 PRG (ug/kg)	Primary Lab MRL (ug/kg)	Primary Lab MDL (ug/kg)	QA Lab MRL (ug/kg)	QA Lab MDL (ug/kg)
Acenaphthene	3.7E+06	330	62.87	33	6.4
Acenaphthylene		330	82.30	33	6.5
Anthracene	2.2E+07	330	51.41	33	7.1
Benzo(a)anthracene	6.2E+02	330	49.03	33	6.5
Benzo(a)pyrene	6.2E+01	330	46.42	33	3.8
Benzo(b)fluoranthene	6.2E+02	330	53.43	33	8.2
Benzo(g,h,i)perylene		330	92.80	33	8.9
Benzo(k)fluoranthene	6.2E+03	330	57.45	33	9.2
Bis(2-chloroethoxy)methane		330	67.56	167	24.8
Bis(2-chloroethyl)ether	2.1E+02	330	71.94	167	40.4
Bis(2-chloroisopropyl)ether	2.9E+03	330	55.90	167	26.7
Bis(2-ethylhexyl)phthalate	3.5E+04	330	65.94	167	70.7
4-Bromophenyl-phenyl ether		330	69.95	167	19.3
Butylbenzylphthalate	1.2E+07	330	42.20	167	24.1
Carbazole	2.4E+04	330	45.54	167	19.4
4-Chloroaniline	2.4E+05	330	22.45	670	72.2
2-Chloronaphthalene	4.9E+06	330	64.02	167	21.7
4-Chlorophenyl-phenyl ether		330	77.29	167	33.8
Chrysene	6.2E+04	330	43.56	33	6.7
Dibenzo(a,h)anthracene	6.2E+01	330	91.90	33	6.7
Dibenzofuran	2.9E+05	330	71.91	167	25.5
3,3'-Dichlorobenzidine	1.1E+03	330	34.17	167	33.4
1,2-Dichlorobenzene	3.7E+05	330	71.30	167	23.3
1,3-Dichlorobenzene	1.6E+04	330	48.04	167	21.7
1,4-Dichlorobenzene	3.4E+03	330	72.02	167	25.4
Diethylphthalate	4.9E+07	330	70.69	167	35.6
Dimethylphthalate	1.0E+08	330	61.73	167	25.2
Di-n-butylphthalate		330	43.74	167	19.5
2,4-Dinitrotoluene	7.2E+02	330	51.19	167	37.6
2,6-Dinitrotoluene	7.2E+02	330	62.29	167	25.1
Di-n-octylphthalate	2.4E+06	330	57.95	167	29.6
1,2-Diphenylhydrazine	6.1E+02	330	69.00	NA	NA
Fluoranthene	2.3E+06	330	59.83	33	6.2
Fluorene	2.7E+06	330	69.53	33	6.3
Hexachlorobenzene	3.0E+02	330	68.56	67	19.1
Hexachlorobutadiene	6.2E+03	330	48.13	167	38.2
Hexachlorocyclopentadiene	3.7E+05	330	34.40	670	114
Hexachloroethane	3.5E+04	330	61.25	167	27

TABLE 3-4 (continued)

Analyte	Region 9 PRG (ug/kg)	Primary Lab MRL (ug/kg)	Primary Lab MDL (ug/kg)	QA Lab MRL (ug/kg)	QA Lab MDL (ug/kg)
Indeno(1,2,3-cd)pyrene	6.2E+02	330	143.17	33	6.6
Isophorone	5.1E+05	330	64.08	167	24.7
2-Methylnaphthalene		330	63.27	167	36.8
Naphthalene	5.6E+04	330	65.93	33	6.6
2-Nitroaniline	1.7E+03	1300	59.93	167	33.7
3-Nitroaniline		1300	167.00	330	43.3
4-Nitroaniline		1300	81.85	330	47.2
Nitrobenzene	2.0E+04	330	62.04	33	9.4
N-Nitroso-di-methylamine	9.5E+00	330	69.87	167	26.7
N-Nitroso-di-n-propylamine	6.9E+01	330	58.66	167	28.7
N-Nitrosodiphenylamine	9.9E+04	330	59.16	167	17
Phenanthrene		330	58.79	33	5.3
Pyrene	2.3E+06	330	59.32	33	7.5
1,2,4-Trichlorobenzene	6.5E+05	330	59.57	167	24.8
Benzoic Acid	1.0E+08	1300	133.00	1670	719
Benzyl alcohol	1.8E+07	330	25.44	330	160
4-Chloro-3-methylphenol		330	63.66	330	54.5
2-Chlorophenol	6.3E+04	330	68.96	167	24.9
2,4-Dichlorophenol	1.8E+05	330	62.26	330	56
2,4-Dimethylphenol	1.2E+06	1300	54.42	330	78.6
4,6-Dinitro-2-methylphenol		1300	20.95	330	96.1
2,4-Dinitrophenol	1.2E+05	330	18.81	670	266
2-Methylphenol	3.1E+06	330	65.05	167	26.9
3 & 4-Methylphenol	3.1E+05	330	75.64	167	32.1
2-Nitrophenol		330	60.48	330	74.9
4-Nitrophenol		1300	47.69	670	186
Pentachlorophenol	3.0E+03	1300	52.82	670	184
Phenol	3.7E+07	330	67.93	167	25.6
2,4,5-Trichlorophenol	6.1E+06	330	85.31	330	73.8
2,4,6-Trichlorophenol	6.1E+03	330	62.14	330	67.7

TABLE 3-5
Soil and Sediment PCB Target Compounds
3540C/8082

Analyte	Region 9 PRG (ug/kg)	Primary Lab MRL (ug/kg)	Primary Lab MDL (ug/kg)	QA Lab MRL (ug/kg)	QA Lab MDL (ug/kg)
Aroclor-1016	3.9E+03	17	8.3	16.7	5.6
Aroclor-1221	2.2E+02	17	8.3	16.7	4.6
Aroclor-1232	2.2E+02	17	8.3	16.7	4.5
Aroclor-1242	2.2E+02	17	8.3	16.7	4.9
Aroclor-1248	2.2E+02	17	8.3	16.7	3.6
Aroclor-1254	2.2E+02	17	8.3	16.7	3.7
Aroclor-1260	2.2E+02	17	8.3	16.7	3.3

TABLE 3-6
Soil and Sediment Nitroaromatic Target Compounds
8330

Analyte	Region 9 PRG (ug/kg)	Primary Lab MRL (ug/kg)	Primary Lab MDL (ug/kg)	QA Lab MRL (ug/kg)	QA Lab MDL (ug/kg)
2,4-Dinitrotoluene	7.2E+02	500	100	100	14.4
2,6-Dinitrotoluene	7.2E+02	500	10	200	25.4
2-Amino-4,6-dinitrotoluene		500	110	200	12.1
4-Amino-2,6-dinitrotoluene		500	100	200	85.6
HMX	3.1E+06	500	100	200	30.2
m-Dinitrobenzene	6.1E+03	500	130	100	5
m-Nitrotoluene	3.7E+05	500	130	200	32.5
Nitrobenzene	2.0E+04	500	100	100	16.9
o-Nitrotoluene	3.7E+05	500	150	200	31.8
p-Nitrotoluene	3.7E+05	500	100	200	30.2
RDX	4.4E+03	500	100	200	33.3
sym-Trinitrobenzene	1.8E+06	500	100	100	14.4
Tetryl		500	100	250	117
Trinitrotoluene, 2,4,6- (TNT)	1.6E+04	500	150	100	15.2

TABLE 3-7
Soil and Sediment Metals Target Compound List
3050B/6010C/7471A

Analyte	Region 9 PRG (ug/kg)	Primary Lab MRL (ug/kg)	Primary Lab MDL (ug/kg)	QA Lab MRL (ug/kg)	QA Lab MDL (ug/kg)
Aluminum	7.6E+07	40,000	10,000	20,000	5050
Antimony	3.1E+04	12,000	2000	2000	430
Arsenic	3.9E+02	1000	300	1000	370
Barium	5.4E+06	40,000	1000	1000	72
Beryllium	1.5E+05	1000	200	400	18
Cadmium	3.7E+04	1000	200	200	58
Calcium	NA	1,000,000	200,000	10,000	1840
Chromium	2.1E+05	2000	1000	1000	100
Cobalt	9.0E+05	10,000	1000	500	120
Copper	3.1E+06	5000	1000	1000	220
Iron	2.3E+07	20,000	10,000	10,000	2200
Lead	4.0E+05	600	300	500	250
Magnesium	NA	1,000,000	200,000	10,000	1010
Manganese	1.8E+06	3000	1000	1000	53
Mercury	2.3E+04	33	13	16.7	6.1
Nickel	1.6E+06	8000	1000	1000	480
Potassium	NA	1,000,000	200,000	50,000	6000
Selenium	3.9E+05	1000	600	1000	450
Silver	3.9E+05	2000	200	500	100
Sodium	NA	1,000,000	200,000	100,000	78,600
Thallium	5.2E+03	500	250	1000	570
Vanadium	5.5E+05	10,000	1000	500	150
Zinc	2.3E+07	4000	2000	2000	1370

TABLE 3-8
Groundwater and Surface Water Volatile Target Compound List
5030/8260B

Analyte	Region 9 PRG (ug/L)	Primary Lab MRL (ug/L)	Primary Lab MDL (ug/L)	QA Lab MRL (ug/L)	QA Lab MDL (ug/L)
Dichlorodifluoromethane	3.9E+02	2.0	.21	1.0	0.12
Chloromethane	1.5E+00	2.0	.47	1.0	0.20
Bromomethane	8.7E+00	2.0	.58	1.0	0.59
Vinyl chloride	2.0E-02	2.0	.24	1.0	0.16
Chloroethane	4.6E+00	2.0	.14	1.0	0.32
Trichlorofluoromethane	1.3E+03	2.0	.20	1.0	0.14
1,1,2-Trichloro-1,2,2-trifluoroethane	5.9E+04	2.0	.20	NA	NA
Methylene chloride	4.3E+00	2.0	.38	1.0	0.24
Acetone	6.1E+02	10.0	1.5	5.0	1.4
Carbon disulfide	1.0E+03	1.0	.34	5.0	0.15
Methyl acetate	6.1E+03	2.0	.50	NA	NA
1,1-Dichloroethene	3.4E+02	1.0	.31	1.0	0.25
1,1-Dichloroethane	8.1E+02	1.0	.18	1.0	0.15
cis-1,2-Dichloroethene	6.1E+01	1.0	.16	1.0	0.20
trans-1,2-Dichloroethene	1.2E+02	1.0	.23	1.0	0.16
Methyl tert-butyl ether	1.3E+01	1.0	.20	1.0	0.21
Chloroform	6.2E+00	1.0	.23	1.0	0.14
1,2-Dichloroethane	1.2E-01	1.0	.21	1.0	0.25
2-Butanone	1.9E+03	10.0	1.02	5.0	1.0
Bromochloromethane		2.0	.21	1.0	0.27
1,1,1-Trichloroethane	3.2E+03	1.0	.18	1.0	0.17
Cyclohexane	3.5E+04	1.0	.13	NA	NA
Carbon tetrachloride	1.7E-01	1.0	.22	1.0	0.34
Bromodichloromethane	1.8E-01	1.0	.21	1.0	0.22
1,2-Dichloropropane	1.6E-01	1.0	.19	1.0	0.19
cis-1,3-Dichloropropene	4.0E-01	1.0	.13	1.0	0.15
Trichloroethene	2.8E-02	1.0	.17	1.0	0.13
Methylcyclohexane	5.2E+03	1.0	.20	NA	NA
Dibromochloromethane	1.3E-01	1.0	.21	1.0	0.22
1,1,2-Trichloroethane	2.0E-01	1.0	.19	1.0	0.24
Benzene	3.4E-01	1.0	.14	1.0	0.23
trans-1,3-Dichloropropene	4.0E-01	1.0	.27	1.0	0.16
Bromoform	8.5E+00	1.0	.20	1.0	0.32
Isopropylbenzene	6.6E+02	1.0	.17	1.0	0.32
4-Methyl-2-pentanone	1.6E+02	5.0	.31	5.0	0.92
2-Hexanone		5.0	.42	5.0	0.99
Tetrachloroethene	6.6E-01	1.0	.31	1.0	0.18
1,2-Dibromoethane	7.6E-04	1.0	.19	1.0	0.33
Toluene	7.2E+02	1.0	.44	1.0	0.44
1,1,2,2-Tetrachloroethane	5.5E-02	1.0	.21	1.0	0.34
Chlorobenzene	1.1E+02	1.0	.11	1.0	0.15

TABLE 3-8 (continued)

Analyte	Region 9 PRG (ug/L)	Primary Lab MRL (ug/L)	Primary Lab MDL (ug/L)	QA Lab MRL (ug/L)	QA Lab MDL (ug/L)
Ethylbenzene	2.9E+00	1.0	.17	1.0	0.21
Styrene	1.6E+03	1.0	.16	1.0	0.18
Xylenes (total)	2.1E+02	1.0	.34	2.0	0.36
1,2-Dibromo-3-chloropropane	4.8E-02	2.0	.15	1.0	0.41
1,3-Dichlorobenzene	5.5E+00	1.0	.15	1.0	0.21
1,4-Dichlorobenzene	5.0E-01	1.0	.14	1.0	0.25
1,2-Dichlorobenzene	3.7E+02	1.0	.15	1.0	0.29
1,2,3-Trichlorobenzene		1.0	.30	1.0	0.43
1,2,4-Trichlorobenzene	1.9E+02	1.0	.30	1.0	0.36

TABLE 3-9
Groundwater and Surface Water Semi-Volatile Target Compound List
3510C/8270C

Analyte	Region 9 PRG (ug/L)	Primary Lab MRL (ug/L)	Primary Lab MDL (ug/L)	QA Lab MRL (ug/L)	QA Lab MDL (ug/L)
Acenaphthene	3.7E+02	5.0	1.0	1.0	0.094
Acenaphthylene		5.0	1.0	1.0	0.078
Anthracene	1.8E+03	5.0	1.0	1.0	0.089
Benzo(a)anthracene	9.2E-02	5.0	1.0	0.2	0.12
Benzo(a)pyrene	9.2E-03	5.0	1.0	0.2	0.16
Benzo(b)fluoranthene	9.2E-02	5.0	1.0	0.2	0.079
Benzo(g,h,i)perylene		5.0	1.0	1.0	0.17
Benzo(k)fluoranthene	9.2E-01	5.0	1.0	0.2	0.1
Bis(2-chloroethoxy)methane		5.0	1.0	2.0	0.31
Bis(2-chloroethyl)ether	9.8E-03	5.0	1.0	2.0	0.32
Bis(2-chloroisopropyl)ether	2.7E-01	5.0	1.0	2.0	0.32
Bis(2-ethylhexyl)phthalate	4.8E+00	5.0	1.0	10	6.6
4-Bromophenyl-phenyl ether		5.0	1.0	5.0	0.96
Butylbenzylphthalate	7.3E+03	5.0	1.0	2.0	0.21
Carbazole	3.4E+00	5.0	1.0	5.0	0.8
4-Chloroaniline	1.5E+02	5.0	1.0	10	1.2
2-Chloronaphthalene	4.9E+02	5.0	1.0	2.0	0.27
4-Chlorophenyl-phenyl ether		5.0	1.0	10	1.2
Chrysene	9.2E+00	5.0	1.0	0.5	0.15
Dibenzo(a,h)anthracene	9.2E-03	5.0	1.0	0.3	0.18
Dibenzofuran	2.4E+01	5.0	1.0	2.0	0.32
3,3'-Dichlorobenzidine	1.5E-01	10	1.0	5.0	0.97
1,2-Dichlorobenzene	3.7E+02	5.0	1.0	2.0	0.33
1,3-Dichlorobenzene	5.5E+00	5.0	1.0	2.0	0.32
1,4-Dichlorobenzene	5.0E-01	5.0	1.0	2.0	0.32
Diethylphthalate	2.9E+04	5.0	1.0	2.0	0.16
Dimethylphthalate	3.6E+05	5.0	1.0	2.0	0.27
Di-n-butylphthalate		5.0	1.0	5.0	1.1
2,4-Dinitrotoluene	9.9E-02	5.0	1.0	1.0	0.27
2,6-Dinitrotoluene	9.9E-02	5.0	1.0	0.5	0.12
Di-n-octylphthalate	1.5E+03	5.0	1.0	10	1.3
1,2-Diphenylhydrazine	8.4E-02	5.0	1.0	NA	NA
Fluoranthene	1.5E+03	5.0	1.0	1.0	0.46
Fluorene	2.4E+02	5.0	1.0	1.0	0.079
Hexachlorobenzene	4.2E-02	5.0	1.0	0.5	0.16
Hexachlorobutadiene	8.6E-01	5.0	1.0	5.0	1.6
Hexachlorocyclopentadiene	2.2E+02	5.0	1.0	20	4.0
Hexachloroethane	4.8E+00	5.0	1.0	5.0	1.8

TABLE 3-9 (continued)

Analyte	Region 9 PRG (ug/L)	Primary Lab MRL (ug/L)	Primary Lab MDL (ug/L)	QA Lab MRL (ug/L)	QA Lab MDL (ug/L)
Indeno(1,2,3-cd)pyrene	9.2E-02	5.0	1.0	0.2	0.19
Isophorone	7.1E+01	5.0	1.0	2.0	0.3
2-Methylnaphthalene		5.0	1.0	0.5	0.08
Naphthalene	6.2E+00	5.0	1.0	1.0	0.085
2-Nitroaniline	1.0E+00	25	1.0	5.0	0.69
3-Nitroaniline		25	1.0	10	0.68
4-Nitroaniline		25	1.0	10	1.5
Nitrobenzene	3.4E+00	5.0	1.0	1.0	0.39
N-Nitroso-di-methylamine	1.3E-03	5.0	1.0	0.5	0.11
N-Nitroso-di-n-propylamine	9.6E-03	5.0	1.0	0.5	0.11
N-Nitrosodiphenylamine	1.4E+01	5.0	1.0	1.0	0.28
Phenanthrene		5.0	1.0	1.0	0.08
Pyrene	1.8E+02	5.0	1.0	1.0	0.077
1,2,4-Trichlorobenzene	1.9E+02	5.0	1.0	2.0	0.28
Benzoic Acid	1.5E+05	25	1.0	20	8.3
Benzyl alcohol	1.1E+04	5.0	1.0	20	3.4
4-Chloro-3-methylphenol		5.0	1.0	10	1.2
2-Chlorophenol	3.0E+01	5.0	1.0	5.0	1.4
2,4-Dichlorophenol	1.1E+02	5.0	1.0	10	1.2
2,4-Dimethylphenol	7.3E+02	5.0	1.0	10	1.2
4,6-Dinitro-2-methylphenol		25	1.0	20	2.1
2,4-Dinitrophenol	7.3E+01	25	10	20	11.5
2-Methylphenol	1.8E+03	5.0	1.0	2.0	0.28
3 & 4-Methylphenol	1.8E+02	5.0	1.0	2.0	0.76
2-Nitrophenol		5.0	1.0	10	1.5
4-Nitrophenol		25	1.0	20	7.8
Pentachlorophenol	5.6E-01	25	5.0	10	1.3
Phenol	2.2E+04	5.0	1.0	5.0	1.3
2,4,5-Trichlorophenol	3.6E+03	5.0	1.0	10	0.97
2,4,6-Trichlorophenol	3.6E+00	5.0	1.0	10	0.79

TABLE 3-10
Groundwater and Surface Water PCB Target Compounds

Analyte	Region 9 PRG (ug/L)	Primary Lab MRL (ug/L)	Primary Lab MDL (ug/L)	QA Lab MRL (ug/L)	QA Lab MDL (ug/L)
Aroclor-1016	9.6E-01	.250	0.120	0.50	0.18
Aroclor-1221	3.4E-02	.250	0.120	0.50	0.42
Aroclor-1232	3.4E-02	.250	0.120	0.50	0.35
Aroclor-1242	3.4E-02	.250	0.120	0.50	0.43
Aroclor-1248	3.4E-02	.250	0.120	0.50	0.48
Aroclor-1254	3.4E-02	.250	0.120	0.50	0.35
Aroclor-1260	3.4E-02	.250	0.120	0.50	0.17

TABLE 3-11
Groundwater and Surface Water Nitroaromatic Target Compounds

Analyte	Region 9 PRG (ug/L)	Primary Lab MRL (ug/L)	Primary Lab MDL (ug/L)	QA Lab MRL (ug/L)	QA Lab MDL (ug/L)
2,4-Dinitrotoluene	9.9E-02*	0.50	0.10	0.31	0.032
2,6-Dinitrotoluene	9.9E-02*	0.50	0.10	0.31	0.071
2-Amino-4,6-dinitrotoluene		0.50	0.11	0.31	0.035
4-Amino-2,6-dinitrotoluene		0.50	0.10	0.31	0.074
HMX	1.8E+03	0.50	0.10	0.31	0.122
m-Dinitrobenzene	3.6E+00	0.50	0.13	0.16	0.033
m-Nitrotoluene	6.1E+01	0.50	0.13	0.31	0.137
Nitrobenzene	3.4E+00	0.50	0.10	0.16	0.032
o-Nitrotoluene	6.1E+01	0.50	0.15	0.31	0.082
p-Nitrotoluene	6.1E+01	0.50	0.10	0.31	0.082
RDX	6.1E-01	0.50	0.10	0.16	0.077
sym-Trinitrobenzene	1.1E+03	0.50	0.10	0.16	0.039
Tetryl		0.50	0.10	0.39	0.065
Trinitrotoluene, 2,4,6- (TNT)	2.2E+00	0.50	0.15	0.16	0.036

* PRG value is the cancer risk PRG for a mixture of DNT isomers. The individual isomer non-cancer PRGs are as follows: 2,4-DNT = 7.3E+01; 2,6-DNT = 3.6E+01.

TABLE 3-12
Groundwater and Surface Water Metals Target Compound List

Analyte	Region 9 PRG (ug/L)	Primary Lab MRL (ug/L)	Primary Lab MDL (ug/L)	QA Lab MRL (ug/L)	QA Lab MDL (ug/L)
Aluminum	3.6E+04	200	50	200	13.3
Antimony	1.5E+01	15	5.0	20	2.8
Arsenic	4.5E-02	10	3.0	10	2.1
Barium	2.6E+03	50	5.0	10	0.32
Beryllium	7.3E+01	5	1.0	4	0.16
Cadmium	1.8E+01	5	1.0	2	0.36
Calcium	NA	2000	500	100	56.9
Chromium	1.1E+02	10	2.0	10	1.3
Cobalt	7.3E+02	12.5	5.0	5	1.2
Copper	1.5E+03	25	4.0	10	2.1
Iron	1.1E+04	100	30	100	33.9
Lead	NA	3.0	1.5	5	2.6
Magnesium	NA	2000	500	100	9.5
Manganese	8.8E+02	15	3.0	10	0.44
Mercury	1.1E+01	0.2	0.08	0.2	0.075
Nickel	7.3E+02	10	3.0	10	1.7
Potassium	NA	2000	500	500	43.2
Selenium	1.8E+02	10	6.0	10	4.2
Silver	1.8E+02	10	1.0	5	0.9
Sodium	NA	2000	500	1000	431
Thallium	2.4E+00	10	3.0	10	4.6
Vanadium	2.6E+02	12.5	5.0	5	1.0
Zinc	1.1E+04	20	5.0	20	6.4

TABLE 3-13
Groundwater Water Quality Analyses

Analyte	Method	Region 9 PRG (ug/L)	Primary Lab MRL (mg/L)	Primary Lab MDL (mg/L)
Turbidity	EPA 180.1		2.0 NTU	1.0 NTU
Alkalinity	EPA 310.1		2	1.0
Hardness	EPA 200.7		2.5	1.3
Total Organic Carbon	SW-846 9060		2.0	0.6
Total Dissolved Solids	EPA 160.1		20	20
Total Suspended Solids	EPA 160.2		4	4
Chloride	EPA 300.0/325.3		0.5	0.2
Total Cyanide	SW-846 9010A/9012	7.3E+02	0.01	0.005
Nitrate	EPA 352.3/353.2	1.0E+04	0.05	0.025
Sulfate	EPA 300.0/375.4		0.5	0.25

Table 3-14
PLUMBROOK ORDNANCE ACID AREAS
Precision and Accuracy Goals

Analysis	QC Check	Acceptance Limits
SW-846 8260B VOCs	GC/MS Tune	BFB tune must meet the ion abundance criteria in the method
	ICAL	SPCC compounds must meet method requirements, and CCCs must have RSD≤ 30%. Other target analytes shall have RSD ≤ 15% (r 0.995 or r2 0.990) or mean RSD for all target analytes ≤ 15% with no individual analytes > 30%.
	ICV (must be second source)	80-120%
	CCV	SPCC compounds must meet method requirements, and CCCs must have D< 20%, mean D ≤20% with a max D for each analyte ≤30%
	Internal Standards	-50% to +100% area of midpoint
	Method Blank	<1/2 MRL
	LCS Recovery	80-120% waters, 75-125% soils
	MS/MSD Recovery	70-130%
	MS/MSD RPD	30% (SPMF 40%)
	Surrogate Recovery	70-130%
SW-846 8270C SVOCs	GC/MS Tune	DFTPP tune must meet the ion abundance criteria in the method
	ICAL	SPCC compounds must meet method requirements, and CCCs must have RSD≤ 30%. Other target analytes shall have RSD ≤ 15% (r 0.995 or r2 0.990) or mean RSD for all target analytes ≤ 15% with no individual analytes > 40%.
	ICV (must be second source)	70-130%
	CCV	SPCC compounds must meet method requirements, and CCCs must have D< 20%, mean D ≤20% with a max D for each analyte ≤30%
	Internal Standards	-50% to +100% area of midpoint
	Method Blank	<1/2 MRL
	LCS Recovery	60-120% waters and soils
	MS/MSD Recovery	45-135%
	MS/MSD RPD	50% for waters, and 60% for soils
	Surrogate Recovery	60-120% for B/N compounds , and 45-135% for Acid compounds

Table 3-14 (continued)

Analysis	QC Check	Acceptance Limits
SW-846 8082 PCBs	ICAL (1016/1260 five points/three peaks per aroclor)	RSD ≤ 20% or r>.99
	ICV (must be second source)	85% to 115%
	CCV	mean D ≤ 15% with no target %D > 30%
	Method Blank	<1/2 MRL
	LCS Recovery	50-130%
	MS/MSD Recovery	40-140%
	MS/MSD RPD	50%
	Surrogate Recovery	40-140%
	Second Column Confirmation	RPD ≤ 40%
SW-846 8330 Explosives	ICAL	RSD ≤ 20% or r>.99
	ICV (must be second source)	85% to 115%
	CCV	mean D ≤ 15% with no target %D > 30%
	Method Blank	<1/2 MRL
	LCS Recovery	60-120%
	MS/MSD Recovery	50-140%
	MS/MSD RPD	50%
	Surrogate Recovery	50% to 150%
	Second Column Confirmation	RPD ≤ 40%
SW-846 6010B ICP Metals	ICAL	r ≥ 0.995
	ICV (must be second source)	90% to 110%
	CCV	90% to 110%
	Blanks (method, calibration,etc.)	<MDL
	ICS	80% to 120%
	LCS Recovery	80%-120%
	Matrix Spike	75% to 125%
	Matrix Duplicate	≤ 25% RPD
	Post Digestion Spike	75% to 125%
	Serial Dilution	4 fold dilution within 10% D of original result
SW-846 7000 Series GFAA Metals	ICAL	r ≥ 0.995
	ICV (must be second source)	80% to 120%
	CCV	80% to 120%
	Blanks (method, calibration,etc .)	<MDL
	LCS Recovery	80% to 120%
	Matrix Spike	75% to 125%
	Matrix Duplicate	≤ 25% RPD
	Post Digestion Spike	75% to 125%
	Serial Dilution	4 fold dilution within 10% D of original result

Table 3-14 (continued)

Analysis	QC Check	Acceptance Limits
SW-846 7470A/7471A Mercury	ICAL	$r \geq 0.995$
	ICV (must be second source)	80% to 120%
	CCV	80% to 120%
	Blanks (method, calibration,etc.)	<MDL
	LCS Recovery	80% to 120%
	Matrix Spike	80% to 120%
	Matrix Duplicate	$\leq$ 25% RPD
Various Wet Chemistry Methods	Calibration	per method
	Calibration Verification	per method
	LCS	50% to 150%
	Method Blank	<1/2 MRL
	MS/MSD Recovery	50% to 150%

Appendix A

APPENDIX A
Laboratory HTRW-CX Certifications

DEPARTMENT OF THE NAVY

NAVAL FACILITIES ENGINEERING SERVICE CENTER
1100 23RD AVE
PORT HUENEME CA 93043-4370

IN REPLY REFER TO:
NFESC 413
October 24, 2006

Mr. Randy Ward
QA Manager
Empirical Laboratory, LLC
227 French Landing Drive
Nashville, TN 37228

Dear Mr. Ward,

This correspondence addresses the status of Empirical Laboratory, LLC of Nashville, Tennessee in the Navy Installation Restoration (IR) Quality Assurance (QA) Program as administered by the Naval Facilities Engineering Service Center (NFESC).

Your laboratory is accepted to perform sample analysis for the methods listed in Table 1. The period of acceptance expires February 28, 2007. This acceptance does not guarantee the delivery of any analytical samples. Acceptance is facility specific and can not be transferred to an affiliated or subcontract laboratory.

The Navy's assessment included a review of the laboratory's QA manual, selected standard operating procedures (SOPs) and SOP master list, list of major analytical instrumentation, performance test (PT) results and onsite assessment documentation[1].

The Navy reserves the right to conduct additional laboratory assessments or to suspend or revoke acceptance status for any or all of the listed parameters if deemed necessary.

Table 1

METHOD	PARAMETER	MATRIX
9056/300 Series	Anions: Chloride, Fluoride, Sulfate, Nitrate, Nitrite, and Ortho-phosphate	Water
9010B/9014	Total Cyanide	Water/Solid
8051A	Organochlorine Herbicides	Water/Solid
7470A/7471A	Mercury	Water/Solid
8260B	Volatile Organic Compounds	Water/Solid
8270C	Semivolatile Organic Compounds	Water/Solid
8330	Nitroaromatics & Nitramines	Water/Solid
8310	Polyaromatic Hydrocarbons	Water/Solid
8081A	Organochlorine Pesticides	Water/Solid

[1] State of New Jersey (Office of Quality Assurance) conducted an on-site assessment under National Environmental Laboratory Accreditation Conference (NELAC) requirements on March 21-23, 2006.

NFESC 413
October 24, 2006

8082	Polychlorinated Biphenyls (PCBs)	Water/Solid
8015B	TPH (GRO/ DRO)	Water/Solid
6010B/7000A	TAL Metals: Aluminum, Antimony, Arsenic, Barium, Beryllium, Boron, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Mercury, Molybdenum, Nickel, Potassium, Silver, Sodium, Strontium, Thallium, Tin, Titanium, Vanadium, and Zinc	Water/Solid
7196A	Hexavalent Chromium	Water/Solid

Acceptance for use for parameters not identified on the table will be determined by Navy project personnel.

The laboratory should notify NFESC if there are parameters not presented on Table 1 that the laboratory expects to run on a routine basis in support of Navy installation restoration projects. In these circumstances the laboratory's capability to run the tests will be reviewed and the table will be modified accordingly.

Questions concerning the information provided should be directed to the NFESC IR QA Program coordinator, Ms. Patricia Moreno at (805) 982-1659, or via email at pati.moreno@navy.mil.

Sincerely,

Robert J. Kratzke
Supervisor, Consultation/Information
Management Branch

DEPARTMENT OF THE NAVY
NAVAL FACILITIES ENGINEERING SERVICE CENTER
1100 23RD AVE
PORT HUENEME CA 93043-4370

IN REPLY REFER TO:

NFESC 413
January 4, 2007

Ms. Marilyn Krueding
Quality Assurance Specialist
Severn Trent Laboratories - Chicago
2417 Bond Street
University Park, IL 60466

Dear Ms. Krueding,

This correspondence addresses the status of Severn Trent Laboratories - Chicago (STL-Chicago) of University Park, IL in the Navy Installation Restoration (IR) Quality Assurance (QA) Program as administered by the Naval Facilities Engineering Service Center (NFESC).

Your laboratory is accepted to perform sample analysis for the methods listed in Table 1. The period of acceptance expires June 15, 2007. This acceptance does not guarantee the delivery of any analytical samples. Acceptance is facility specific and can not be transferred to an affiliated or subcontract laboratory.

The Navy's assessment included a review of the laboratory's QA manual, selected standard operating procedures (SOPs) and SOP master list, list of major analytical instrumentation, performance test (PT) results and onsite audit documentation[1].

The Navy reserves the right to conduct additional laboratory assessments or to suspend or revoke acceptance status for any or all of the listed parameters if deemed necessary.

Table 1

METHOD	PARAMETER	MATRIX
300 Series/9056	Anions: Ammonia, Bromide, Chloride, Nitrate, Nitrite, O-Phosphate, Fluoride, Sulfate, Total Phosphorous, Sulfide, and Total Kjeldahl Nitrogen	Water
6010B	TAL Metals: Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Potassium, Selenium, Silver, Sodium, Thallium, Vanadium, and Zinc	Water/Solid

[1] State of Illinois, Department of Health Services, Environmental Laboratory Accreditation Program (ELAP), conducted an on-site assessment under National Environmental Laboratory Accreditation Conference (NELAC) requirements on July 25-27, 2006.

7000 Series	Mercury, Antimony, Arsenic, Selenium, Thallium, Cadmium, Chromium, and Lead	Water/Solid
7196A	Hexavalent Chromium	Water/Solid
8015B	TPH - Gasoline Range Organics/Diesel Range Organics	Water/Solid
8081A	Organochlorine Pesticides by GC	Water/Solid
8082	Polychlorinated Biphenyls (PCBs) by GC	Water/Solid/Oil
8260B	Volatile Organic Compounds by GC/MS	Water/Solid
8270C	Semivolatile Organic Compounds by GC/MS	Water/Solid
8310	Polynuclear Aromatic Hydrocarbons by HPLC	Water/Solid
8330	Analysis of Explosives by HPLC	Water/Solid
9014/9010B	Cyanide	Water/Solid
9060	Total Organic Carbon (TOC)	Water/Solid
9066	Phenolics	Water
9071B/1664A	Oil & Grease	Water

Acceptance for use for parameters not identified on the table will be determined by Navy project personnel.

The laboratory should notify NFESC if there are parameters not presented on Table 1 that the laboratory expects to run on a routine basis in support of Navy installation restoration projects. In these circumstances the laboratory's capability to run the tests will be reviewed and the table will be modified accordingly.

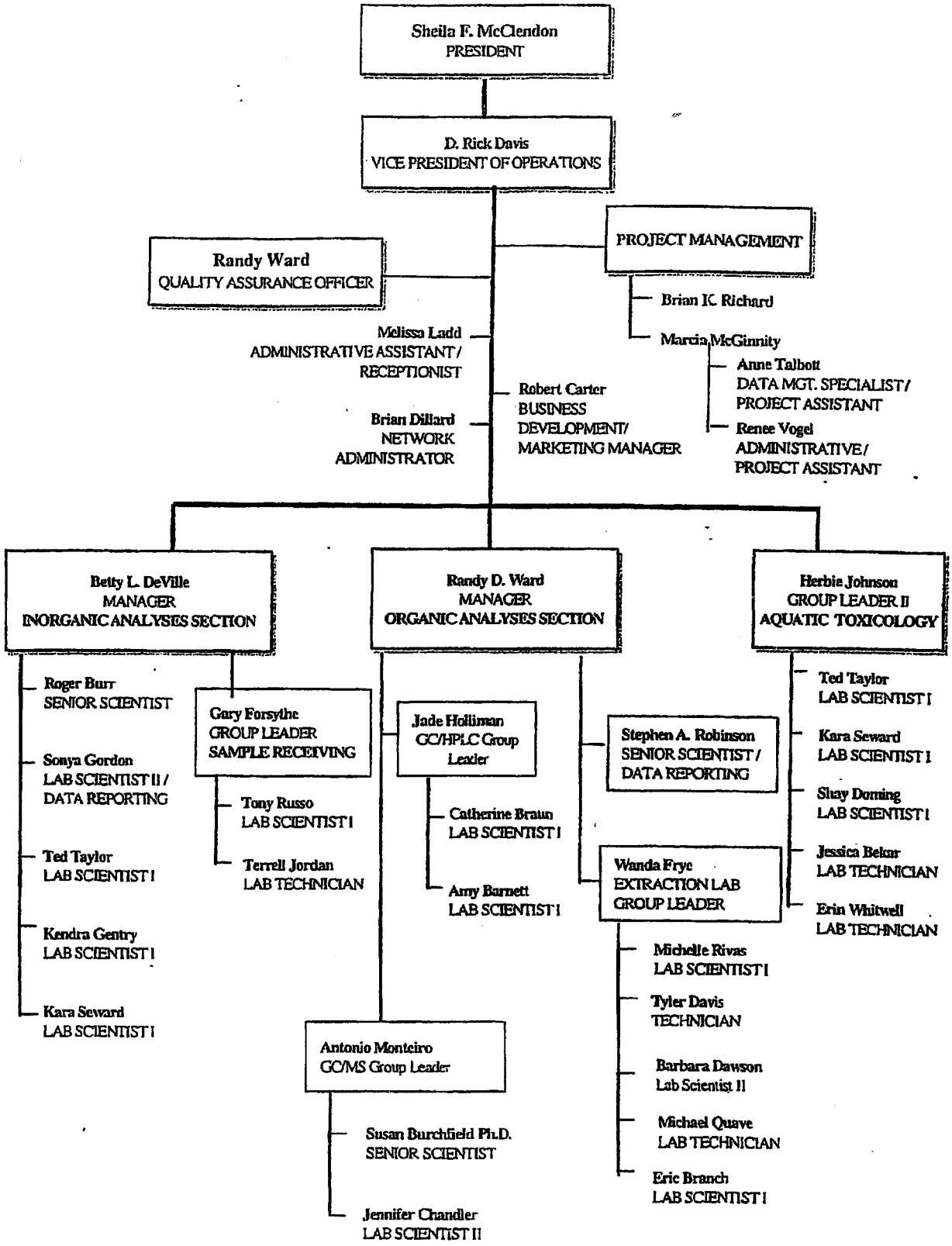
Questions concerning the information provided should be directed to the NFESC IR QA Program coordinator, Ms. Patricia Moreno at (805) 982-1659, or via email at pati.moreno@.navy.mil.

Sincerely,

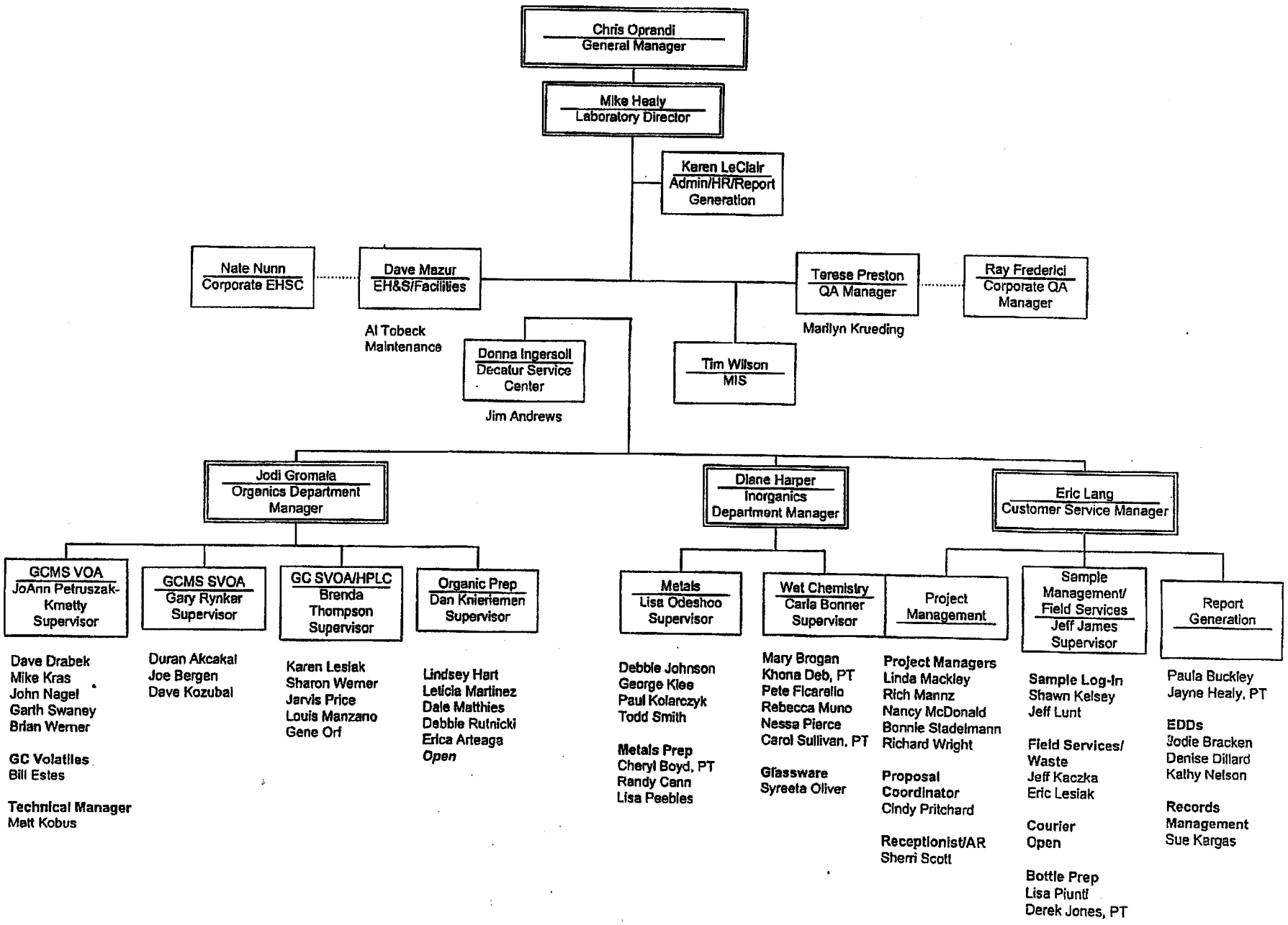
Robert J. Kratzke
Supervisor, Consultation/Information
Management Branch

Appendix B

APPENDIX B
Laboratory Organizational Charts


Sheila F. McClendon
PRESIDENT
D. Rick Davis
VICE PRESIDENT OF OPERATIONS
Randy Ward
QUALITY ASSURANCE OFFICER
PROJECT MANAGEMENT
Brian IC Richard
Marcia McGinnity
Anne Talbott
DATA MGT. SPECIALIST/
PROJECT ASSISTANT
Renee Vogel
ADMINISTRATIVE/
PROJECT ASSISTANT
Melissa Ladd
ADMINISTRATIVE ASSISTANT/
RECEPTIONIST
Brian Dillard
NETWORK
ADMINISTRATOR
Robert Carter
BUSINESS
DEVELOPMENT/
MARKETING MANAGER
Betty L. DeVille
MANAGER
INORGANIC ANALYSES SECTION
Randy D. Ward
MANAGER
ORGANIC ANALYSES SECTION
Herbie Johnson
GROUP LEADER II
AQUATIC TOXICOLOGY
Roger Burr
SENIOR SCIENTIST
Sonya Gordon
LAB SCIENTIST II/
DATA REPORTING
Ted Taylor
LAB SCIENTIST I
Kendra Gentry
LAB SCIENTIST I
Kara Seward
LAB SCIENTIST I
Gary Forsythe
GROUP LEADER
SAMPLE RECEIVING
Tony Russo
LAB SCIENTIST I
Terrell Jordan
LAB TECHNICIAN
Jade Holliman
GC/HPLC Group
Leader
Catherine Braun
LAB SCIENTIST I
Amy Barnett
LAB SCIENTIST I
Antonio Monteiro
GC/MS Group Leader
Susan Burchfield Ph.D.
SENIOR SCIENTIST
Jennifer Chandler
LAB SCIENTIST II
Stephen A. Robinson
SENIOR SCIENTIST/
DATA REPORTING
Wanda Frye
EXTRACTION LAB
GROUP LEADER
Michelle Rivas
LAB SCIENTIST I
Tyler Davis
TECHNICIAN
Barbara Dawson
Lab Scientist II
Michael Quave
LAB TECHNICIAN
Eric Branch
LAB SCIENTIST I
Ted Taylor
LAB SCIENTIST I
Kara Seward
LAB SCIENTIST I
Shay Doming
LAB SCIENTIST I
Jessica Bekur
LAB TECHNICIAN
Erin Whitwell
LAB TECHNICIAN

Seasern + Treat



Appendix C

APPENDIX C
Laboratory SOPs

SOP No.	Revision No.	Date	Page
UGE-8082	06	03/24/06	1 of 31

TITLE: Gas Chromatography - Semi-Volatiles Analysis of PCBs by SW-846 Method 8082

Updated by:	Signature:	Date:
Brenda Thompson Chemist, Organics Dept.	Brenda Thompson	3-20-06

Approved by:	Signature:	Date:
Patti J. Gibson Section Manager, Organics Dept.	Patti Gibson	3-20-06
David W. Mazur Env. Health & Safety Coor.	D.W. Mazur	3/20/06
Terese A. Preston Quality Manager	Terese A. Preston	3/21/06

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1.0 SCOPE / APPLICATION

This method is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in assorted matrices by SW-846 Methods 8000B & 8082.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

Specific requirements pertaining to the DoD QSM Version 3.0 are located in Attachment 6.0. These requirements are additionally applicable to all NFESC projects. Any deviations from these procedures and/or variances from must be addressed appropriately in accordance with standard operating protocol and pre-approved on a project by project basis.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified annually.

1.1.2 Reporting Limits

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values ~2-5x the respective MDL to ensure confidence in the value reported. Client specific requests for reporting to MDL are special circumstances not to be confused with the previous statement. Attachment 1 provides a list of compounds analyzed by this method and their reporting limits.

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.2 Summary of Method

This method provides the gas chromatographic (GC) conditions and necessary standardization procedures for the detection of parts per billion (ppb) levels of Aroclors. The appropriate sample extraction must be performed prior to sample analysis (Refer to Section 7.3.1).

2.0 INTERFERENCES

2.1 Phthalates

Interference's by phthalate esters can pose a problem in PCB analysis. These compounds generally appear in the chromatogram as large late-eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Avoiding contact with any plastic materials can best minimize interferences from phthalates.

2.2 Co-extractions

Co-extracted interferences will vary considerably from sample to sample. Clean-ups are available to help eliminate or lessen interferences. All extracts analyzed for PCBs routinely receive a sulfuric acid cleanup. Additionally, florisil clean-ups, sulfur clean-ups, and GPC clean-ups may be performed (Refer to USP-003 for complete details).

2.3 Glassware

All glassware/equipment used in the preparation of standards (volumetric flasks, pipettes, beakers, eppendorf tips) are rinsed well with the appropriate solvent and allowed to dry before use. After completion of standard preparation, unused amounts of standards are properly disposed of, and all glassware/equipment rinsed well with the appropriate solvent. Rinse/excess solvent is properly collected and disposed of. These procedures should eliminate positive interferences from these sources.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

- PCBs are a bio-accumulating carcinogen. Extreme care should be taken when working with this material.
- Interior parts of GC's can be very hot. Care should be taken if adjusting instrument.

3.2 Primary Material Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

4.1 Gas Chromatographs

Gas Chromatographs (GC) are equipped with dual electron capture detectors (ECDs) (Ni_{63}). Each GC is equipped with an autosampler and uses TurboChrom for data acquisition and Target for processing data.

4.2 Column - Megabor

- RTX-5, 0.53 mm ID, 30 m length, temperature limits of -20°C to 260°C < 310°C, and 0.5 - 1.0 micron film thickness (or equivalent).
- RTX-35, 0.53 mm ID, 30 m length (or equivalent)
- RTX-CLPesticides2, 0.53 ID, 30 m length, maximum temperature of 330°C. Film thickness of 0.42 micron (or equivalent).
- Guard Column - Phenyl-methyl deactivated 5 meter, 0.53 mm I.D. (or equivalent).

Similar columns can be used if all QC criteria can be met.

5.0 REAGENTS AND STANDARDS

A label on any reagent bottle must contain the concentration of the reagent, name of the reagent, date prepared, expiration date and the analyst who prepared the reagent. Standard labels will additionally contain the standard log number for that particular standard.

All standards and spikes must be stored at 4±2°C in glass bottles with Teflon-lined lids. The standard log number must also be indicated on the bottle label.

5.1 Solvents

Hexane, Acetone, Isooctane.....Pesticide quality or better.

5.2 Intermediate Standards

All standards used are certified. The Aroclor 1016 and 1260 used for the initial calibration are verified against an alternate source [Second Source Verification (SSV)]. Aroclor standards are purchased as solutions at a level of ~1000 ug/mL. Appropriate dilutions are prepared such that the intermediate standards are at a level of 5.0 ug/mL in Hexane for all Aroclors (1016, 1221, 1232, 1242, 1248, 1254 and 1260). Aroclor 1016 and 1260 are added together into the same intermediate solution and is referred to as AR1660.

The surrogate compounds, Decachlorobiphenyl (DCB) and 2,4,5,6-Tetrachloro-m-xylene (TCX), are purchased as a solution at a level of ~200 ug/mL. An intermediate standard is made at concentrations of the surrogates in the intermediate standard are at 2.0 ug/mL (1 mL to 100 mL FV) in Hexane. Intermediate standard solutions must be replaced 6 months from the date of preparation.

5.3 Calibration Standards

A standard containing a mixture of Aroclor 1016 and Aroclor 1260 (AR1660) will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. Working calibration standards are prepared in Hexane from the intermediate solutions. At least 5 levels of AR1660 are required, however, generally 6 levels are prepared. Concentrations range from 0.025 ng/uL to 1.00 ng/uL (Table 1). The five concentration levels are prepared through dilutions of the intermediate standards with hexane. One of the concentration levels should be at or below the established reporting limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.4 Surrogates

The analyst must monitor the performance of the extraction, clean-up (when used), analytical system and the effectiveness of the method for each sample matrix by spiking each sample, matrix spike (MS), MS duplicate (MSD), laboratory control sample (LCS) and method blank (MB) with the surrogates. The surrogates used are Decachlorobiphenyl (DCB) and 2,4,5,6-Tetrachloro-m-xylene (TCX).

6.0 CALIBRATION

Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument. Preparation of all reference materials used for calibration must be documented.

Calibration pertains to both primary and secondary columns. Establish GC operating parameters equivalent to those indicated in Section 7.4.1. Prepare calibration standards using the procedures indicated in Section 5.3.

Calibration Controls	Sequence	Control Limit
Initial Calibration Standards	6 pt. curve of AR1660 prior to samples	≤20% RSD (alternatively, if the correlation coefficient is >0.99, linear regression may be used).
Second Source Verification (SSV) [1]	After initial calibration	± 15% Difference
Cont. Calib. Verif. (CCV) [2,3]	After initial calibration, Every 10 samples*	± 15% Difference
Retention Time Windows	After initial calibration, Every 10 samples*	3 X Std. Deviation

[1] The SSV concentration corresponds to Level 4 of the linearity standards (Table 1).
[2] The CCV concentration is varied throughout the analytical sequence at concentrations that correspond to the Level 3 and 4 of the linearity standards (Table 1).
[3] The CCV is required at least once per 20 samples; however, it is strongly recommended that it be analyzed after every 10 samples, to reduce the number of reanalyses if the CCV is out-of-control.

6.1 External Standard Calibration

6.1.1 Prepare calibration standards as described in Section 5.3. Because of the sensitivity of the ECD, the injection port and column should always be cleaned prior to performing the initial calibration. When PCBs are to be quantitatively determined as Aroclors, the initial calibration consists of two parts.

6.1.1.1 As noted in Section 5.3, a standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other 5 Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample. Therefore, an initial 5-point calibration is performed using the mixture of Aroclors 1016 and 1260 described in Section 5.3.

6.1.1.2 Standards of the other five Aroclors are necessary for the pattern recognition. These standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the AR1660 mixture has been used to describe the detector response. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the 5 AR1660 standards.

6.1.1.3 Specific clients/projects/agency protocol may include the requirement of full 5-point initial calibrations for one or all of the additional Aroclors. In these cases (example DOD/NFESC) the specific Aroclor will be quantitated from the 5-point curve versus a single-point.

6.1.2 Record the peak area (or height) for each characteristic Aroclor peak to be used for quantitation. A minimum of 3 peaks, preferably 5 peaks, must be chosen for each Aroclor. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor.

6.1.3 Calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the equation below:

$$\text{Calibration Factor (CF)} = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

Five sets of calibration factors will be generated for the AR1660 mixture, each set consisting of the calibration factors for each of the 3-5 peaks chosen for this mixture. The single standard for each of the other Aroclors will generate at least 3 calibration factors, one for each selected peak.

6.2 Retention Time Windows

Absolute retention times are used for the identification of PCBs as Aroclors. However, in addition to retention times, peak patterns play a large roll in the identification of Aroclors.

Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

6.2.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make 3 injections of all standard mixtures throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in retention time windows that are too tight.

6.2.2 Record the retention time for 3 to 5 major peaks for both Aroclor 1016 and Aroclor 1260 to 3 decimal places. Calculate the mean and the standard deviation of the 3 absolute retention times.

6.2.3 If the standard deviation of the retention times for a target compound is 0.000 (no difference between the 3 retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

6.2.4 The width of the retention time window is defined as $\pm$3x the standard deviation of the absolute retention times. If the default standard deviation is employed, the width of the window will be 0.03 minutes.

6.2.5 Establish the center of the retention time windows from the calibration verification at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration. Retention time windows can be updated every 12 hours. However, they are usually only updated at the onset of a continuing calibration sequence or after maintenance has been performed.

6.2.6 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory and available for review.

6.2.7 The laboratory monitors the retention time for both surrogates throughout the analytical sequence.

7.0 PROCEDURE

7.1 Quality Control Checks

The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 samples	< Reporting Limit
LCS	1 in 20 samples	Stat. Control Limits (Attachment 1)
LCD [1]	1 in 20 samples	Stat. Control Limits (Attachment 1)
Matrix Spike (MS)	1 in 20 samples	Stat. Control Limits (Attachment 1)
MS Duplicate (MSD)	1 in 20 samples	Stat. Control Limits (Attachment 1)
Surrogate	every sample	At least 1 within statistical limits.

[1] LCD is required only when insufficient sample is available for the MS/MSD or as requested by the client/project.

7.2 Sample Preservation and Storage

All samples should be collected in a glass container with a Teflon-lined lid. If the lid does not have a Teflon-liner, aluminum foil should be placed between the jar and lid (dull side facing sample). All samples should be refrigerated (4 ± 2°C) up until extraction; as well as all extracts up until analysis.

Matrix	Reference	Preservation	Holding Time: To Extract (VTS)	Holding Time: After Extr. to Analysis
Soil/Sediment	\	\	14 days	\
Water	SW-846	Cool, 4 ± 2°C	7 days	40 days
Waste/Oil	/	/	14 days	/

VTS = verified time of sampling

7.3 Sample Preparation

7.3.1 Extraction Procedure

The matrix determines which extraction procedure to follow. Waters are extracted following the separatory funnel method (SOP No. USP-3510) or continuous liquid-liquid method (USP-3520); soils are extracted by sonication (USP-3550) or soxhlet (USP-3541); and wastes and oils are by dilution (USP-3580).

7.3.2 Clean-up Procedure

Various clean-up procedures are available if interferences are present. A sulfuric acid cleanup is always performed on all PCB extracts. A sulfur cleanup using elemental Mercury is used to eliminate sulfur interference in extracts as needed. A Florisil cleanup and a GPC cleanup may also be used (USP-003).

7.4 Calibration / Standardization

7.4.1 GC Conditions

- Carrier Gas (Helium) 3 - 10 mL/min
- Make up Gas (Nitrogen) > 60 mL/min
- Column Temp Program 70 - 285°C (based on elution profile)
- Ramp 5-40°C/min
- Injector Temp 220°C and/or Cool on Column
- Detector Temp 350°C

These conditions are subject to change based on instrument performance. The oven temperature and carrier gas flow may vary slightly between instruments and columns.

7.4.2 Verification of Calibration Curve

Verify calibration each 12-hour shift by injecting calibration verification standards prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every 20 samples (after every 10 samples is recommended to minimize the number of samples requiring re-injection when QC limits are exceeded) and at the end of the analysis sequence. For Aroclor analyses, the calibration verification standard should be a mixture of AR1660. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclor after the AR1660 mixture used for calibration verification throughout the analytical sequence.

7.4.2.1 The calibration factor for each analyte calculated from the calibration verification standard (CCV) must not exceed a difference of more than ±15% when compared to the mean calibration factor from the initial calibration curve.

$$\% \text{ Difference} = \frac{CF_{ccv} - \text{Mean CF}}{\text{Mean CF}} \times 100$$

Where:
CF_{ccv} = CF of the CCV
Mean CF = Mean CF from the ICAL.

7.4.2.2 If this criterion is exceeded for any calibration factor, inspect the GC to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis. If routine maintenance does not return the instrument performance to meet the QC requirements based on the last initial calibration, then a new initial calibration must be performed.

7.4.2.3 Calibration Evaluation and Acceptance Criteria

Refer to the STL Corporate Procedure, P-T-001, 'Selection of Calibration Points' (Attachment 2) or on STLs Intranet.

7.5 Qualitative identification

Qualitative identifications of target analytes are made by examination of the sample chromatograms versus the standard chromatograms from the initial calibration. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area when overlapping peaks cause errors in area integration.

7.5.1 Each sample analysis must be bracketed with an acceptable initial calibration, verification standard(s) (each 12-hour shift), or calibration standards interspersed within the samples. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that met the QC criteria must be re-injected.

7.5.2 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative or quantitative QC criteria are exceeded.

7.5.3 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out-of-control; however, pattern recognition is critical in determining the presence of Aroclors in associated samples. Determine the cause of the retention time shift and correct the problem.

7.5.4 The identification of Aroclors using this method is based predominantly on peak patterns. In addition, to a lesser degree, agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards is utilized. Tentative identification of an Aroclor occurs when a specific pattern of peaks from a sample extract matches the specific pattern of peaks observed in a standard. Again, peak pattern plays a large part in determining the presence of Aroclors in samples. All tentative identifications are confirmed using a second GC column of dissimilar stationary phase if required, based on a clearly identifiable Aroclor pattern, or using another technique such as GC/MS.

7.5.5 Since the calibration standards are analyzed on both columns, the results for both columns must meet the calibration acceptance criteria. If the peak pattern on both columns match an Aroclor pattern, then the target analyte identification has been confirmed.

7.6 Quantitation of PCBs as Aroclors

The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

7.6.1 Use the individual Aroclor standards (not the AR1660 mixtures) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

7.6.2 Once the Aroclor pattern has been identified, compare the responses of 3 to 5 peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen in Section 6.1 and the calibration model (linear or non-linear) established from the multi-point calibration of the AR1660 mixture. A concentration is determined using each of the characteristic peaks and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

7.6.3 Weathering of PCBs in the environment and changes resulting from waste treatment processed may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. The quantitation of Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs of the basis of retention times should be subtracted from the total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

7.6.4 Manual Integration Policy

In each case where the file has been edited or manual integrations have been performed the operator must identify, initial, and date the changes on the hardcopy report. The following guidelines apply:

- Manual integrations should be consistent between all files integrated.
- Manual integrations should not be performed to meet QC criteria.
- Manual integrations are automatically flagged with an 'M' on the raw data.
- Excessive manual integrations may reflect an instrumental or methodological problem that should be addressed.
- Manual integrations shall follow the STL Corporate SOP for manual integrations (#S-Q-004) located in Attachment 5, with example case narrative.

Manual integrations are most often performed for the following reasons:

- Assignment of correct peak that was mis-identified by the data system.
- Incomplete auto-integration due to high level of target compound detected.
- Incomplete auto-integration due to background interference.
- Incorrect auto-integration due to co-elution or near co-elution of compounds.
- Missed peaks.

PCB manual integrations are rare. However, if required must follow the Corporate SOP as attached. Additionally, documentation of the presence or absence of such shall be incorporated into the Case Narrative (if so required by the client/project). All integrations

are reviewed by the analyst. All chromatograms and reports are printed after any integrations take place and are routinely included in the data packages.

7.7 Preventive Maintenance

- The septa should be changed between each analyses sequence. The number of injections made plays a part in how frequently they should be changed. Generally, not more than 100-150 injections should be made without changing the septum.
- The entire system including Nitrogen and Helium tanks should be periodically checked for leaks and frayed wires.
- Leak tests must be performed every six months on every ECD.

7.7.1 Suggested Maintenance

When any calibration, QC sample or analytical sample is outside the acceptance criteria, one or more of the following actions may be necessary.

- Inspect injection end of column for particulates and/or cracks.
- Condition the column - upper end of column temperature 285°C for 1 - 2 hours.
- Remove 1-6 inches from the injector and guard column. (if present)
- Make sure septum doesn't need to be changed.
- Change single-tapered liner (w/glass wool)

Refer to the instrument manuals if problems are encountered which can not be solved by routine maintenance.

7.8 Gas Chromatographic Analysis

7.8.1 Prior to initial calibration or continuing calibration if the instrument has been idle for a period of time, several primes shall be analyzed to prepare the inlet, column and 'Y' (if applicable) by removing possible active sites from these surfaces. The prime shall be 10X the AR1660CCV4 level (mid-point) and 20X the AR1660CCV3 level. This is equivalent to a concentration of 5.0 ug/mL each component AR1016 and AR1260. Priming the instrument at this level has been successful at removing active sites and higher concentrations of the primes do not appear to be necessary.

7.8.2 **Direct Injection** - For a capillary column, inject 1 - 2 uL of the sample extract using a solvent flush technique equipped with the autosampler.

7.8.3 If the response of a sample exceeds the linear range of the system dilute the extract and reanalyze. Over lapping peaks are not always evident when peaks are off scale. The computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.8.4 If peak detection is prevented by the presence of interferences, further clean-up may be required.

7.8.5 Standards must be injected at the intervals no more than every 20 samples; however, it is recommended that no more than 10 samples be analyzed between CCVs. The calibration factor for each CCV must not exceed a 15% difference when compared to the initial calibration. When this criterion is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary. The instrument must be in-control before proceeding with sample analysis. All samples that were injected after the last in-control CCV must be re-injected. If routine maintenance does not return the instrument back into control based on the last initial calibration, verify that proper maintenance has been performed and if still out-of-control start a new initial calibration.

8.0 QUALITY CONTROL

8.1 QC Summary

For each analytical batch (20 samples), a MB, LCS, MS and MSD must be analyzed. If a MS/MSD is not performed, either because of insufficient sample volume, or the client specifically requests that a MS and MSD not be performed, then a LCS duplicate (LCD) is extracted. The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps. Also, every sample must be spiked with the surrogates TCX and DCB. These results are tabulated by the QA/QC to generate in-house control limits.

8.1.1 The MB will be examined to determine if contamination is being introduced in the laboratory.

8.1.2 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

8.1.3 Precision will be measured by the reproducibility of the MSs and will be calculated as Relative Percent Difference (RPD). If MSs were not analyzed, reproducibility will be measured using the LCS/LCD. Results must agree within statistical control limits in order to be considered acceptable.

8.1.4 Surrogate compounds will be added to every sample to measure performance of the analysis. Results must agree within statistical control limits in order to be considered acceptable. However, if DCB recovery is low or compounds interfere with DCB, then the TCX should be evaluated for acceptance. Proceed with corrective action when both surrogates are outside of control limits.

8.1.5 Each time an analytical sequence is started, the first Aroclor 1660 must be evaluated to determine if the chromatographic system is operating properly. The analyst should consider:

- Do the peaks look normal?
- Is the response obtained comparable to the response from previous calibrations?

Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc.

8.1.6 Required Instrument QC

8.1.6.1 Section 6.0 requires that the %RSD $\leq$ 20% when comparing calibration factors to determine if the initial calibration curve is linear.

8.1.6.2 Section 6.0 sets a limit of $\pm$15% difference when comparing the continuing response of AR1660 versus the initial response. If the limit is exceeded, corrective action must be taken to correct the problem or the sequence must be started over. All samples following the last standard that was in-control must be reanalyzed.

8.1.6.3 Section 6.2 requires the establishment of retention time windows.

8.1.6.4 Section 7.4.2 sets a limit of $\pm$15% difference when comparing the initial response of the initial linearity to any succeeding standards analyzed during an analytical sequence.

8.1.6.5 Section 7.5.5 requires that all succeeding standards in an analytical sequence must fall within the daily retention time window established by the first standard of the sequence.

8.1.7 For every batch of samples (20 samples = a batch) the analyst must perform a MS, MSD, MB, and LCS. Also, every sample, and QC sample must be spiked with the surrogates.

8.1.7.1 The desired concentrations of the spikes used are as follows:

Compound	Water (ug/mL)	Soil/Sediment (ug/mL)	Waste/Oil (ug/mL)
AR 1660	5.0	5.0	50.0
TCX	0.40	0.40	4.0
DCB	0.40	0.40	4.0

*Surrogates are prepared in separate solutions from the MS compounds. Refer to the SOP for the preparation of standards and QC solutions.

8.1.8 Limits used for spike recoveries are in-house statistically generated control limits, or limits which have been specifically assigned by the client. If statistical data is not available due to lack of data points, default limits of 50-150% are used until enough data points are available. Refer to the backlog for the requested control limits (see also the QAP, when appropriate).

8.1.9 If a recovery is outside of its control limits, the result should first be examined for any possible calculation errors. If that isn't the problem, then the sample should be re-injected. If after re-injecting the sample it is still out-of-control, and the LCS is in-control, the out-of-control recovery may be attributed to the matrix.

8.2 Corrective Actions

When an out-of-control situation occurs, the analysts must use his/her best analytical judgment and available resources when determining the action to be taken. The out-of-control situation may or may not be caused by more than one problem. The analyst should seek the help of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out-of-control situation and the required corrective action. The analysis must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out-of-control situation should be reanalyzed. Out-of-control data must never be released without approval of the supervisor, QA personnel or the lab manager's approval.

Listed below are steps to be taken by the analyst when an out-of-control situation occurs:

- demonstrate that all the problems creating the out-of-control situation were addressed;
- document the problem and the action which was taken to correct the problem on a corrective action report (CAR) form;
- document on the corrective action report that an in-control situation has been achieved;
- receive approval (signature) of the section manager, QA personnel, or the laboratory manager prior to the release of any analytical data associated with the problem.

Whenever a problem exists, such as insufficient sample to run MSs and MSDs, a Sample Discrepancy Report (SDR) is written. It is filed with the report discussing the actions taken to correct and document the problem. The analyst and their section manager decide what to do with this problem, whether it is analytical, sampling, or matrix interference.

Listed below are some suggested courses of action that may be taken to correct out-of-control situations that may occur with the procedure.

8.2.1 Initial Calibration Curve

For external standard calibration, it is required that a 5-point linearity be run initially (Section 6.1). If the percent relative standard deviation (%RSD) of the calibration factor is $\leq$ 20% for the linearity over the working range, linearity through the origin can be assumed, and the average calibration factor (CF) may be used for calculations. If an individual RSD is >20%, but the average across all analytes is <20%, analysis may continue. Care should be taken when using this approach because if hits are detected in the sample, the result may be biased if it's individual RSD was >20%. Alternatively, if the correlation coefficient is >0.99, linear regression may be used.
Prior to running a new calibration, or preparing new standards, ensure proper maintenance has been performed. Correct the problem, then re-run the calibration curve and determine new response factor.

8.2.2 Initial Calibration Verification (SSV)

The CF of the initial calibration check standard must not vary from the Average CF of the calibration curve by more than $\pm$ 15% on both columns. Repeat the standard to verify proper preparation. If still non-compliant, prepare a new standard from the original stock, recalibrate with a new standard curve, or prepare new stock and/or working standards.

8.2.3 Continuing Calibration Verification (CCV)

The response factors of the initial calibration check standard must not vary from the Average CF of the calibration curve by more than $\pm$ 15% on both columns, the average % difference across all analytes may be used. Care should be taken when using this approach because if hits are detected in the sample, the result may be biased if its individual %D was >15%. If the average response for all analytes is $\pm$15%, then calibration has been verified. If the average % difference is >15%, corrective actions must be taken in order to bring the instrument back into control, or a new calibration curve must be analyzed. If any of the target compounds fail the criteria, then the standard is considered to be non-compliant. If the standard is non-compliant, then reanalyze the standard. If the standard is still non-compliant, remove 3-6 inches from the guard column and condition the column for 1-2 hours. If the standard is still non-compliant, then prepare a new standard. If the new standard is non-compliant, then recalibrate the instrument with a new curve. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard than last met the QC criteria must be re-injected. If a CCV is biased high and all associated samples are clean then this failed criteria should be narrated as showing increased sensitivity, and how this might bias data.

8.2.4 Method Blank (MB)

The MB should not contain any target compounds at or above the reporting limit. If non-compliant, then the MB should be reanalyzed to determine if instrument contamination was the cause. If the MB is still non-compliant and the samples are within the extraction holding time, then request re-extraction using an SDR and reanalyze all associated samples containing target compounds at <10x amount found in the MB. If a sample contains target compounds at ≥ 10x amount found in the MB, or if target compounds are not detected in the sample, then that sample does not require re-extraction and the results may be reported without qualification. If the samples are outside the extraction holding time, then contact the project manager using an SDR. If samples are re-extracted beyond the required holding time, results for both analyses will be reported.

8.2.5 Laboratory Control Sample (LCS)

The recoveries for the spiked compounds must be within statistical (or otherwise specified) limits. If non-compliant, check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze the LCS to determine if instrumental conditions or analytical preparation was the cause. If the LCS is still non-compliant notify the Project Manager using an SDR, to determine if re-extraction is required of all associated samples. If samples are re-extracted beyond the required holding time, results for both analyses will be reported.

8.2.6 Laboratory Control Sample Duplicate (LCD)

The LCD must meet all control limits as LCS in addition to limits set for precision (same corrective action as the LCS).

8.2.7 Matrix Spike (MS)

The recoveries for the spiked compounds should be within statistical control limits. If non-compliant, check calculations and spike preparation for documentable errors. If no errors are found, and the associated LCSs are within advisory limits, then sample matrix effects are the most likely cause.

8.2.8 Matrix Spike Duplicate (MSD)

See MS for recoveries. RPDs should be within statistical limits. If non-compliant, check calculations for documentable errors. Check unspiked sample results and surrogate recoveries for indications of matrix effects. If significant differences exist between the MS and MSD, reanalysis of the sample spikes may be necessary.

8.2.9 Surrogate Spike

Both recoveries for the surrogate(s) should be within control limits. If non-compliant, check calculations and spike preparation for documentable errors. If no errors are found, and the surrogate recoveries in the MB and LCSs are within statistical limits, then sample matrix effects are the most likely cause. Any samples with both surrogate recoveries outside statistical limits with, no visible chromatographic cause, should be reanalyzed to determine if an injection error was the cause for the out-of-control recovery. If the surrogate recoveries in the associated MB and LCS are not within advisory limits, and the samples are within the extraction holding time, then re-extract and reanalyze all associated samples. If the samples are outside the extraction holding time, then contact the project manager using and SDR. If samples are re-extracted beyond the required holding time, results for both analyses will be reported.

8.2.10 Retention Time Windows

Evaluate the data for usability based on a comparison with the standards run during the analytical sequence. Also, consider the retention times for the surrogates and spiked compounds analyzed before and after the sample in question.

Initial retention time windows must be established following the procedure described in Section 6.2. Daily windows are then established as in Section 6.2.5 at the beginning of each analytical sequence. If a continuing standard is outside of their daily windows, corrective actions must be taken before continuing. Check the septa first and make sure it is tight before any other possibilities are investigated. Check the press connectors, discoloration of the guard column or check the carrier gas and its connection to the instrument for possible leaks.

Perhaps baking the detector at 350°C for about an hour or two will help.

IF AT ANY TIME THE ANALYST IS UNCERTAIN AS TO WHAT ACTIONS TO TAKE OR HOW TO PERFORM SUGGESTED MAINTENANCE, PLEASE SEE YOUR SECTION MANAGER. IF SOMETHING UNUSUAL IS HAPPENING THAT IS NOT DESCRIBED IN THIS SECTION, SEE YOUR SECTION MANAGER. COSTLY (AS IN MONEY AND TIME) DAMAGE CAN RESULT TO THE INSTRUMENT, DETECTOR, OR COLUMN IF MAINTENANCE IS NOT PERFORMED CORRECTLY.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Concentration (ppb) = $\frac{(A_1)(V_t)(Df)}{[(V_i)(V_s)(D)][CF]}$

Where:
A_1 = response for the analyte in the sample (area or height)
V_i = volume of extract injected (mL).
Df = dilution factor (if applicable)
V_t = volume of total extract (mL).
V_s = volume/weight of sample extracted
D = (100 - % Moisture) / 100
CF = Average calibration factor from the initial calibration curve

9.2 %RSD = $\frac{\text{Standard Deviation}}{\text{Mean}} \times 100$

Where,
Standard Deviation = $\frac{\left| \sum_{i=1}^{n} (x_i - \bar{x})^2 \right|^{1/2}}{n - 1}$

Where,
x_1 = each individual value used to calculate the mean
$\bar{x}$ = the mean of n values
n = the total number of values

9.3 % Difference = $\frac{\text{Avg. CF - CF}}{\text{Avg. CF}} \times 100$

Where:
Avg CF = Average CF from initial linearity
CF = CF from the analysis of the verification standard

9.4 Surrogate Percent Recovery = $\frac{Q_d}{Q_a} \times 100$

Where:
Q_d = Quantity determined by analysis
Q_a = Quantity added to sample/blank

9.5 Spike Recovery = $\frac{SR}{SA} \times 100$

Where:
SR = Spike result
SA = Spike added

9.6 Accuracy: $\%R = \frac{(A_T - A_0)}{A_F} \times 100$

Where:
A_T = Total amount recovered in fortified sample
A_0 = Amount recovered in unfortified sample
A_F = Amount added to sample

9.7 Precision: $\%D = \frac{|B_1 - B_2|}{\text{Mean of } B_1 \text{ \& } B_2} \times 100$

Where:
B_1 = %Recovery MS (or LCS)
B_2 = %Recovered MSD (or LCD)

9.8 Instrument Run-Logs

The analysis of samples and standards is documented within each instrument-specific run log, and must be completed for each day's analysis (Attachment 3).

9.9 Traceability of Standards

Upon receipt or preparation, each standard is entered into LIMS and is issued a unique ID# based upon the type and sequential order in which the item was received. Further information includes the manufacturer, lot # (if applicable), the date received or prepared, the expiration date, volume/weight received; concentration (if applicable); preparation details (if applicable), initials of the recording analyst, and the description of the item (i.e., **XXXX** Stock Solution – LCS/MS). Once the record is created, a unique label is printed and affixed to the appropriate standard/reagent container.

9.10 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews according to the criteria established on the data review checklist (Attachment 4). Upon the first 100% review, the checklist is initialed and dated as reviewed. The package, with its checklist, comments and any CARs or SDRs is submitted to the section manager or peer reviewer for a second review. Once again, the checklist is initialed and dated by the second reviewer. The completed data review checklist remains on file with the original data.

10.0 WASTE MANAGEMENT AND POLLUTION PREVISION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Sample vials are placed in the drum labeled "Flammable vials" for disposal, unless they have a high known or historical PCB concentration.
- Expired primary and working PCB standards and sample extracts that have a known or historically high concentration of PCB will be placed in the waste drum labeled "PCB waste".
- Single component standards will be turned over to the EHSC or Waste Technician.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

Table 1. Working Standard Solutions and Concentrations
Table 2. Example: Analytical Sequence

Attachment 1. Example: Target Compounds, Reporting Limits and Statistical Control Limits
Attachment 2. STL Corporate Procedure, P-T-001, 'Selection of Calibration Points'
Attachment 3. Example: Analysis Run Log / Maintenance Log
Attachment 4. Example: Data Review Checklist
Attachment 5. STL Corporate SOP, S-Q-004, Acceptable Manual Integration Practices
Attachment 6. Requirements for DoD QSM Version 3.0

Historical File:
Revision 00: 02/16/98
Revision 01: 02/26/99
Revision 02: 09/20/00
Revision 03: 02/06/02
Revision 04: 07/17/03
Revision 05: 03/01/05
Revision 06: 03/16/06

Reason for Change; Revision 06:

- Annual Review –
- Added Attachment 5 STL Corporate SOP, S-Q-004 and edited Section 7.6.4
- Added Attachment 6 for DoD QSM requirements and appended Section 1.0.
- Changed Section 6.1.1.3 to comply for DoD requirements
- Updated Section 7.7 minor text changes
- Updated Section 8.2.3 minor text changes

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Table 1.

Working Standard Solutions and Concentrations

Compound	Approximate Concentrations (ng/uL)					
	Level 1	Level 2	Level 3[2]	Level 4[1]	Level 5	Level 6
Aroclor-1016	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1221	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1232	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1242	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1248	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1254	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1260	0.025	0.040	0.250	0.500	0.750	1.00

These Individual Solutions must all have DCB and TCX in them. Aroclor 1016 and 1260 are prepared in the same solution and are referred to as AR1660. Unless otherwise specified, only AR1660 needs to be run at least 5 levels to establish linearity. A single point standard is required for the other Aroclors, at the mid-level range (0.50 ng/uL).

[1] Concentration of the first CCV; and the SSV.
[2] Alternating concentration of the CCV.

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LINEARITY CONCENTRATIONS
ng/ul for 6 point calibrations 8080/608/8082

COMPOUNDS	L#1	L#2	L#3	L#4	L#5	L#6
AR1016 (1660)	0.0250	0.0400	0.2500	0.5000	0.7500	1.0000
AR1221				0.5010		
AR1232				0.5000		
AR1242	0.0250	0.0401	0.2505	0.5010	0.7514	1.0019
AR1248				0.5016		
AR1254	0.0251	0.0401	0.2508	0.5016	0.7524	1.0032
AR1260 (1660)	0.0250	0.0400	0.2500	0.5000	0.7500	1.0000
AR1268				0.5020		
TCX	0.002	0.004	0.010	0.020	0.060	0.100
DCB	0.002	0.004	0.010	0.020	0.060	0.100

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updated: 1/20/05

Table 2.

Example: Analytical Sequence

Quantitation & Confirmation of Aroclors			
1.	AR 1660-6	1.	AR 1660-6
2.	AR 1660-5	2.	AR 1660-5
3.	AR 1660-4	3.	AR 1660-4
4.	AR 1660-3	4.	AR 1660-3
5.	AR 1660-2	5.	AR 1660-2
6.	AR 1660-1	6.	AR 1660-1
7.	AR 1254-4	7.	AR 1254-4
8.	AR 1248-4	8.	AR 1248-4
9.	AR 1242-4	9.	AR 1242-4
10.	AR 1232-4	10.	AR 1232-4
11.	AR 1221-4	11.	AR 1221-4
12.	AR1660 CCV-4	12.	AR1660 CCV-4
13.	AR 1660-SSV	13.	AR 1660-SSV
14-23.	Samples	14-23.	Samples
24.	AR1660-CCV-3	24.	AR1660-CCV-3
25-34.	Samples	25-34.	Samples
35.	AR1660 CCV-4	35.	AR1660 CCV-4

NOTE: AR1660 linearity is sufficient for initial calibration of all Aroclors since they include all congeners present in the different regulated Aroclors.

Attachment 1.

Example: Target Compounds, Reporting Limits and Statistical Control Limits

Method Limit Report using report code 8082

Test Long Description	TMX	Units	MDL	RL	Limits LCSLL	LCSUL	LCSRPD	SLL	SUL
Method: PCB Analysis (8082)									
Aroclor 1016		ug/L	0.18	0.50	66	106	20		
Aroclor 1221		ug/L	0.42	0.50					
Aroclor 1232		ug/L	0.35	0.50					
Aroclor 1242		ug/L	0.43	0.50	50	150	20		
Aroclor 1248		ug/L	0.48	0.50					
Aroclor 1254		ug/L	0.35	0.50	50	150	20		
Aroclor 1260		ug/L	0.17	0.50	71	116	20		
Aroclor 1268		ug/L	0.50	0.50					
Decachlorobiphenyl (surr)		ug/L						20	145
PCB, Total (Sum of Aroclors)		ug/L	0.17	0.50					
Tetrachloro-m-xylene (surr)		ug/L						20	144
~~Aroclor 1016~~		~~ug/L~~	0.18	0.50	66	106	20		
Aroclor 1221		ug/L	0.42	0.50					
Aroclor 1232		ug/L	0.35	0.50					
Aroclor 1242		ug/L	0.43	0.50	50	150	20		
Aroclor 1248		~~ug/L~~	0.48	0.50					
Aroclor 1254		ug/L	0.35	0.50	50	150	20		
Aroclor 1260		ug/L	0.17	0.50	71	116	20		
Aroclor 1268		ug/L	0.50	0.50					
Decachlorobiphenyl (surr)		ug/L						20	145
PCB, Total (Sum of Aroclors)		ug/L	0.17	0.50					
~~Tetrachloro-m-xylene (surr)~~		~~ug/L~~						20	144
Aroclor 1016	TCLP Le	ug/L	5.0	50.					
Aroclor 1221	TCLP Le	ug/L	5.0	50.					
Aroclor 1232	TCLP Le	ug/L	5.0	50.					
Aroclor 1242	TCLP Le	ug/L	5.0	50.					
Aroclor 1248	TCLP Le	ug/L	5.0	50.					
Aroclor 1254	TCLP Le	ug/L	5.0	50.					
Aroclor 1260	TCLP Le	ug/L	5.0	50.					
Aroclor 1268	TCLP Le	ug/L	5.0	50.					
Decachlorobiphenyl (surr)	TCLP Le	ug/L							
PCB, Total (Sum of Aroclors)	TCLP Le	ug/L	5.0	50.					
Tetrachloro-m-xylene (surr)	TCLP Le	ug/L							
Aroclor 1016	Filter	ug/Filter	0.50	0.50					
Aroclor 1221	Filter	ug/Filter	0.50	0.50					
Aroclor 1232	Filter	ug/Filter	0.50	0.50					
Aroclor 1242	Filter	ug/Filter	0.50	0.50					
Aroclor 1248	Filter	ug/Filter	0.50	0.50					
Aroclor 1254	Filter	ug/Filter	0.50	0.50					
Aroclor 1260	Filter	ug/Filter	0.50	0.50					
Aroclor 1268	Filter	ug/Filter	0.50	0.50					
Decachlorobiphenyl (surr)	Filter	ug/Filter							

Method Limit Report using report code 8082

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
Method: PCB Analysis (8082)									
PCB, Total (Sum of Aroclors)	Filter	ug/Filter	0.50	0.50					
Tetrachloro-m-xylene (surr)	Filter	ug/Filter							
Aroclor 1016	Oil	ug/Kg	250.	500.	70	112	30		
Aroclor 1221	Oil	ug/Kg	250.	500.					
Aroclor 1232	Oil	ug/Kg	250.	500.					
Aroclor 1242	Oil	ug/Kg	250.	500.					
Aroclor 1248	Oil	ug/Kg	250.	500.					
Aroclor 1254	Oil	ug/Kg	250.	500.					
Aroclor 1260	Oil	ug/Kg	250.	500.	74	116	30		
Aroclor 1268	Oil	ug/Kg	250.	500.					
Decachlorobiphenyl (surr)	Oil	ug/Kg						55	153
PCB, Total (Sum of Aroclors)	Oil	ug/Kg	250.	500.					
Tetrachloro-m-xylene (surr)	Oil	ug/Kg						34	161
Aroclor 1016	Solid	ug/Kg	6.9	16.7	62	107	30		
Aroclor 1221	Solid	ug/Kg	4.8	16.7					
Aroclor 1232	Solid	ug/Kg	2.9	16.7					
Aroclor 1242	Solid	ug/Kg	3.2	16.7	50	150	30		
Aroclor 1248	Solid	ug/Kg	3.5	16.7					
Aroclor 1254	Solid	ug/Kg	4.4	16.7	50	150	30		
Aroclor 1260	Solid	ug/Kg	5.2	16.7	69	116	30		
Aroclor 1268	Solid	ug/Kg	16.7	16.7					
Decachlorobiphenyl (surr)	Solid	ug/Kg						54	128
PCB, Total (Sum of Aroclors)	Solid	ug/Kg	2.9	16.7					
Tetrachloro-m-xylene (surr)	Solid	ug/Kg						49	125
Aroclor 1016	Wipe	ug/Wipe	0.32	0.50	62	108	30		
Aroclor 1221	Wipe	ug/Wipe	0.25	0.50					
Aroclor 1232	Wipe	ug/Wipe	0.25	0.50					
Aroclor 1242	Wipe	ug/Wipe	0.25	0.50					
Aroclor 1248	Wipe	ug/Wipe	0.25	0.50					
Aroclor 1254	Wipe	ug/Wipe	0.25	0.50					
Aroclor 1260	Wipe	ug/Wipe	0.32	0.50	67	115	30		
Aroclor 1268	Wipe	ug/Wipe	0.25	0.50					
Decachlorobiphenyl (surr)	Wipe	ug/Wipe						56	178
PCB, Total (Sum of Aroclors)	Wipe	ug/Wipe	0.25	0.50					
Tetrachloro-m-xylene (surr)	Wipe	ug/Wipe						58	119
Aroclor 1016	3541 So	ug/Kg	5.6	16.7	52	105	30		
Aroclor 1221	3541 So	ug/Kg	4.6	16.7					
Aroclor 1232	3541 So	ug/Kg	4.5	16.7					
Aroclor 1242	3541 So	ug/Kg	4.9	16.7	50	150	30		
Aroclor 1248	3541 So	ug/Kg	3.6	16.7					
Aroclor 1254	3541 So	ug/Kg	3.7	16.7	50	150	30		
Aroclor 1260	3541 So	ug/Kg	3.3	16.7	63	122	30		

Method Limit Report using report code 8082

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
Method: PCB Analysis (8082)									
Aroclor 1268	3541 So	ug/Kg	16.7	16.7					
Decachlorobiphenyl (surr)	3541 So	ug/Kg						70	125
PCB, Total (Sum of Aroclors)	3541 So	ug/Kg	3.3	16.7					
Tetrachloro-m-xylene (surr)	3541 So	ug/Kg						44	135

Attachment 2.

STL Corporate Procedure, P-T-001, 'Selection of Calibration Points'

Approvals and Signatures

Senior Vice President & Chief Operating Officer:	Dr. Keith C. Wheatstone	Date: 10/6/2004
Vice President, Client and Operations Services:	Dr. Charles W. Carter	Date: 10/6/2004
Technology Director:	Dr. Richard Burrows	Date: 9/8/2004

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1.0 PURPOSE

This policy describes Severn Trent Laboratories (STL) requirements for determination of the number of points, and removal of points from calibration curves.

2.0 SCOPE

Applies to all multi-level initial calibrations.

3.0 POLICY

3.1 If the number of data points required for an initial calibration is defined in the method, Quality Assurance (QA) plan, published report, or previously approved Standard Operating Procedure (SOP) that is what will be used.

3.2 In the cases not defined in Section 1, the number of data points will be determined by the technical director based on the Data Quality Objectives (DQOs) for precision and accuracy to be met by the method.

Examples:

A. Need to analyze a new pesticide in water and a published method does not exist. The data will be used to screen samples by UV-HPLC at a waste site for further remediation, using DQOs that require precision/accuracy of ± 50%.

The Technical director selects 2 data points to represent the range of the expected concentration of pesticide and based on 4 Laboratory Control Samples (LCS), the recoveries ranged from 78-104%. Therefore, 2 data points are sufficient for initial calibration for this method.

NOTE: Calibration curves with less than 3 points should only be used after discussion with the client that the data quality objectives will be met.

B. Same compound as above but being measured in laboratory for meeting regulatory limit of 0.05 mg/L in water. Precision and accuracy of ± 20% required.

A five-point calibration is used, based on similar requirements in published methods with similar objectives and the high level of precision and accuracy required.

As noted above for methods where technical director selects the number of data points to meet DQOs for precision and accuracy, the 4 LCS used in the demonstration of capability will be used to assure those DQOs are met. The SOP will then be approved by the Quality Assurance (QA) Manager.

3.3 Removal of Points from a Calibration Curve

3.3.1 Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted unless an injection or instrument problem confined to that point can be clearly documented as described below. Removal of points for individual analytes from levels other than the highest and lowest is not permitted in any event.

3.3.2 If the analyst can document that a level is not valid because of an injection or instrument problem confined to that run, the level may be excluded if the curve still has sufficient levels, or the run may be repeated once only. The whole level (all compounds) must be

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removed or replaced. The curve is evaluated with the level removed or replaced. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve reanalyzed. Corrective action may include, but is not limited to, instrument maintenance and/or re-preparation of standards.

3.3.3 One of the following conditions must be satisfied to allow removal or replacement of a level:

- The data file is corrupted and unusable or the run is interrupted before completion.
- The analyst observes and documents a problem such as leaking of a purge vessel.
- For internal standard methods, the recovery of the internal standards is less than 70% or greater than 130% of the recovery in the other standards, or the amount of analyte recovered is less than 70% or greater than 130% of the expected values (indicating an improperly made up standard).
- For external standard methods, the unit response of the analyte is less than 70% or greater than 130% of the average unit response for the analyte in the other calibration standards (indicating an improperly prepared standard or bad injection).

3.3.4 When using autosamplers with discrete sample pathways for different samples (such as 16 port purge and trap autosamplers) the level to be replaced must be reanalyzed on the same port or that port must be excluded from sample analysis until corrective action is performed and verified by successful analysis of a continuing calibration standard on that port.

3.3.5 The reason for replacing the level **must** be documented in the run log. The fact that the curve passes criteria with the level removed is **not** alone sufficient evidence to document an injection or instrument problem confined to the level.

3.3.6 Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed then the reporting limit is raised to be equivalent to the lowest level used in the calibration curve. In any event the number of levels remaining in the calibration must be at least that required by the method.

3.3.7 Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method.

4.0 RESPONSIBILITIES

All STL associates utilizing methods involving multi-point calibrations are required to follow this policy.

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5.0 ATTACHMENTS

Not Applicable.

6.0 REVISION HISTORY

Revision 3: Updated by Richard Burrows, Technology Director; 9/8/2004.
Section 3.2: Amended 'NOTE'.
Section 3.3.3, bullet #4, text reworded for clarification.

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Attachment 3.

Example: Analysis Run Log / Maintenance Log

GC/ECD Analysis Log - PCB

Page #:_____

GC Conditions: Initial Initial Hold Rate Final Final Hold
Temperature Prog. (1/2): _____ _____ _____ _____ _____
psi _____ Detector Temperature _____ deg. C ICAL Reference_____

Analyst:			Instrument ID#: 41		Date:	
Sample File ID#	Rep#	Method	Sample Description	D.F.	Injection Date/Time	Comments

Reviewer's Signature:_____ Date:_____

GC/ECD Analysis Log - PCB

Page #:_____

GC Conditions: Initial Initial Hold Rate Final Final Hold
Temperature Prog. (1/2): _____ _____ _____ _____ _____
psi _____ Detector Temperature _____ deg. C ICAL Reference_____

Analyst:			Instrument ID#: 42		Date:	
Sample File ID#	Rep#	Method	Sample Description	D.F.	Injection Date/Time	Comments

Reviewer's Signature:_____ Date:_____

STL Chicago
GC Extractables Instrument Maintenance Log

Page No.:_____
Instrument No.:_____

Routine/Informal Maintenance includes: Glass Y-connectors checked for leaks; Periodic system check for leaks, frayed wires and a general overview; and Air and hydrogen ratios checked.

Entry No.:_____

Date of Maintenance:_____ Analyst:_____

___ Septa Changed (~100 injections)
___ Heated the Column/Detector for Cleaning
___ Injection Liner Changed
___ Y-connectors changed
___ Column Changed / Clipped (circle one)
___ O-rings Replaced
___ Other (explain)

Explain/Actions Taken:_____

Demonstration of Control:
___ CCV analyzed and in-control.
___ Samples Reanalyzed.
___ Other (explain)

Explain:_____

Entry No.:_____

Date of Maintenance:_____ Analyst:_____

___ Septa Changed (~100 injections)
___ Heated the Column/Detector for Cleaning
___ Injection Liner Changed
___ Y-connectors changed
___ Column Changed / Clipped (circle one)
___ O-rings Replaced
___ Other (explain)

Explain/Actions Taken:_____

Demonstration of Control:
___ CCV analyzed and in-control.
___ Samples Reanalyzed.
___ Other (explain)

Explain:_____

Reviewer Signature:_____ Date:_____

Attachment 4.

Example: Data Review Checklist

STL Chicago
EGC / HPLC / GC VOA DATA REVIEW CHECKLIST

Site Name:_____ Primary Reviewer:_____ Review Date:_____
JOB Number:_____ Secondary Reviewer:_____ Review Date:_____
No. of Samples/Matrix: a) ____ WATER b) _____ SOIL c) _____ TCLP / SPLP d) _____ Other (_____)
Review Level: a) Full b) Cursory Method: a) GC VOA _____ b) GC _____ c) HPLC _____ d) Other (_____)
Extr. Method: a) SW 3510 b) SW 3520 c) SW 3550 d) SW 3580 e) SW 3541 f) SW 5030 /5035 g) CLP____ h) Other (_____)

CAR's _____ Std. Traceability _____ TASK		PRI REV	SEC REV	COMMENTS
LAB CHRON:	1) Matches Raw Data (Form 4, 8)			
	2) Samples which were Re-Analyzed or Re-Extracted were Re-Logged into LabNet			
	3) Sample Hold Times were Met			
	4) Proper Prep Links were created			
PROJ. REQ.MET:	1) List of Compounds			
	2) Sample Detection Limits Met			
	3) Method Blank Detection Limits Met			
LabNet Batch Status Report Displays Data at RVWD Status Incomplete JOB Status Report reveals no Outstanding Data				
FORM 1:	1) Matches Quant Report			
	2) Matches LabNet Report			
FORM 2: Surrogate Recoveries Within Limits Statistical Limits _____ Method Limits _____ Project Limits _____ (S-F10 used to Clone By Project)				
FORM 3: MS/MSD Recoveries Acceptable Statistical Limits _____ Method Limits _____ Project Limits _____(S-F10 used to Clone By Project)				
FORM 3: BS Recoveries Acceptable Statistical Limits _____ Method Limits _____ Project Limits _____ (S-F10 used to Clone By Project)				
Initial Calibration Criteria Met				
Daily Calibration (CCV) Criteria Met				
Form 10:	1) Retention Window (RT) Criteria Met			
	2) Concentrations Correct			
Correct Usage of FLAGS				
RAW DATA:	1) Raw Data Verified/Complete			
	2) Raw Data Matches Forms			
NARRATIVE:	1) Holding Times			
	2) Method References			
	3) % Recoveries / RPD's			
	4) Analytical Difficulties/Typos			

COMMENTS ON REVERSE

COMMENTS:

REVIEW CYCLE	REASON
1	
2	
3	
4	

STL Chicago
GC/HPLC Data Review Checklist - "CLP-like"
(SW-846 and 40 CFR)

Client: _____ **JOB#:** _____ **Test:**

Reviewer(1): _____ **Date:**

Reviewer(2): _____ **Date:**

COC/Deliverable

Reviewer 1	Reviewer 2	
____	____	Chain-of-custody has been checked to ensure that the proper analyte list is reported.
____	____	All special project requirements are met, i.e., control limits, forms, etc...

Comments: _____

Updating Results in Labnet

____	____	Reagent codes are correct.
____	____	Batch test results match quant. reports.
____	____	Batch cloned for project limits.
____	____	Proper prep links were created (including TCLP link).
____	____	Each required target compound displays "0" when data is reported.
____	____	Client information has been checked for correct list, reporting limits, special requirements.
____	____	Job Notes (CTRL F12) for the job have been reviewed.

Form 1/Associated Data

____	____	Observe chromatograms, check for obvious chromatography errors.
____	____	Check form information for correctness (JOB #, reporting limit, dilution factor, matrix, flags, etc....)
____	____	Check values reported. In an "E" is present, there must be another dilution; if a value is reported, review the chromatogram; if a "J" is reported, review the chromatogram; if an "I" is reported, there must be another dilution run.
____	____	Check that all JOB #'s on the chromatograms match quant report and data on quant report is correct.
		Check that confirmation chromatograms agree with quantitation chromatograms.
____	____	All method blanks are clean.
____	____	All OPC file information is present and correct (matrix, final volume, %sol present for soils).
____	____	Before and after chromatograms are present for all Manual integrations and are dated/initialed by analyst.

Comments: _____

Form 2/Associated Data

____	____	Requested surrogates were used.
____	____	All surrogate recoveries are within control limits. If not, proper corrective actions have been taken and are documented. [Samples with surrogates outside of control limits may not require re-analysis but must be evaluated, flagged, and discussed in the case narrative. If not specified by the client, both (if applicable) surrogate recoveries must be within statistical control limits. Surrogates associated with the method blank and blank spikes should be within control.]
____	____	Confirm all samples and QC for that batch are represented.
____	____	Confirm correct matrix.
____	____	Correct surrogate concentration used for calculating % Recovery. Verify calculations.

Comments: _____

Form 3/Associated Data

Reviewer 1	Reviewer 2	
____	____	Blank spike and blank spike duplicate have the proper batch number, and the proper matrix
____	____	All blank spike/blank spike duplicate recoveries and RPDs are within control limits. If not, proper corrective actions have been taken and documented. Flag outliers for the Case Narrative and provide documentation.
____	____	Confirm that the matrix spike and matrix spike duplicate data correlates with the unspiked analysis.
____	____	All matrix spike/matrix spike duplicate recoveries and RPDs are within control limits. If not, proper corrective actions have been taken and documented. Flag outliers for the Case Narrative.
____	____	Confirm correct matrix and sample ID.
____	____	Correct spike concentration used for calculating % Recovery. Verify calculations.

Comments:_____

_____

Form 4/Associated Data

____	____	Check all header information, extraction date, analysis date and time, instrument and column IDs.
____	____	Confirm all samples associated with the blank are present.
____	____	Confirm all blank summaries are present for all samples/matrices in the data package.
____	____	Confirm proper matrix and extraction method.
____	____	Sulfur cleanup performed (not applicable to some methods)

Comments:_____

_____

Endrin/DDT Breakdown

____	____	All breakdown criteria is met (<15% for DDT and/or Endrin) for 608 and 8081A only.

Comments:_____

_____

Initial Calibration/Associated Data (Form 6)

____	____	Method SW-846: All % RSDs are <20% (5-pt. minimum)
____	____	Method 40CFR: All %RSDs are <10% (3-pt. minimum).
____	____	Recalculate a few %RSDs.
____	____	All header information is correct (times, dates).
____	____	Second Source Verification (SSV) is in control (85%-115%)

Comments:_____

_____

Continuing Calibration Verification/Associated Data (Form 7) - Standards that are outside the control limits must be approved by the Section Manager prior to the reporting of any data.

____	____	All header information is correct. Dates and times of initial standards and continuing standards are correct.
____	____	All retention times are within their windows, those that are outside are marked for Case Narrative.
____	____	Ave. CFs match from ICAL (Form 6) Ave CFs.
____	____	All %Ds are within control limits. If not, proper corrective actions have been taken and documented.
____	____	All Form 7's associated with the samples and QC are present.

Comments:_____

_____

Form 10/Associated Data

Reviewer 1	Reviewer 2	
____	____	Confirm that all analytes which are reported as being detected on the Form 1 are present.
____	____	Confirm that all retention times of analytes reported as positive hits are within their retention time window, and if they aren't, why the analyst reported them must be documented in the comment section.
____	____	The GC columns are marked Y/N for quantitation/confirmation (applicable to 8330 only).

Comments:_____

_____

Additional Data

____	____	All necessary runlogs are present and contain the proper sequences.
____	____	All necessary extraction records are present.
____	____	All required holding times were met for samples dilutions and QC.
____	____	Chronology of data is correct.
____	____	Dates and times of analysis are correct.
____	____	Verify samples are quantitated using the proper ICAL.

Comments:_____

_____

____ RG LabChron/Report Review Initial/Date _____

Project: _____ **Job #:**_____ **Method:**_____

Reviewer (1):_____ **Date:**_____

Reviewer (2):_____ **Date:**_____

Sublist:_____
Instruments (Primary/Confirmation):_____
Cleanups:_____
CAR (Y/N):_____

Target Review

Reviewer 1	Reviewer 2	
____	____	Chromatography is acceptable.
____	____	Chromatograms are scaled properly.
____	____	All peaks are labeled properly.
____	____	All initial calibrations are within control limits ($\leq$ 20% RSD; Correlation Coefficient $\leq$ 0.995).
____	____	Second Source Verification is in control (85% - 115%).
____	____	All continuing calibrations are within control limits ($\pm$ 15% difference).
____	____	All retention times are within their windows.
____	____	All method blanks are clean.
____	____	Calculations verified.
____	____	Verify samples are quantified using the proper ICAL.
____	____	Before and after chromatograms produced for all manual integrations.

Comments:_____

Updating Results in LabNet

____	____	Reagent codes are correct.
____	____	Batch test results match quant reports.
____	____	Batch cloned for project limits.
____	____	Proper prep links were created (including TCLP link).
____	____	Each required target compound diplays "0" when data is reported.
____	____	Client information has been checked for correct list, reporting limits, special requirements.
____	____	Job notes (CTRL F12) for the job have been reviewed.

Comments:_____

GC/HPLC Data Review Checklist

QC Data

____ ____ All LCS/LCD recoveries (and RPDs) are within the required control limits (verify calc.).
____ ____ All surrogate recoveries are within the required control limits (verify calc).
____ ____ All MS/MSD recoveries and RPDs are within the required control limits (verify calc.).

Comments:_____

Note: Anything out of the ordinary must be commented on and be approved by the Unit Leader/Section Manager for inclusion in the Case Narrative.

____ RG LabChron/Report Review Initial/Date _____

Comments:

Attachment 5.

STL Corporate SOP, S-Q-004, 'Acceptable Manual Integration Practices'

STL Chicago
PCB Case Narrative

[redacted] – DO 51, 33, 61
Job #: 233854-1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 14, and 15
PCBs

1. STL Chicago used the following Gas Chromatographic systems for the analysis of PCBs:

ID#	INSTRUMENT	COLUMN TYPE	DETECTOR
31	HP 6890	Rtx-5 (Primary)	Electron Capture

2. The water samples were extracted based on SW846 method 3520. The soil samples were extracted based on SW846 method 3550. All extracts were analyzed for PCBs based on SW846 method 8082. All extracts received a sulfuric acid cleanup and soil extracts were given a GPC cleanup in order to reduce matrix interference.

3. All required holding times were met for the extraction and analysis.

4. The method blanks were below the reporting limits for all Aroclors.

5. The surrogate compounds used for this analysis were Decachlorobiphenyl (DCB) and Tetrachloro-m-xylene (TCX). All surrogate recoveries were within required control limits except sample 233854-11, which had DCB with 33% recovery. Sample was re-analyzed with similar results. No further action was taken.

6. A solution containing Aroclor 1016 and Aroclor 1260 was used for spiking.

7. All blank spike and blank spike duplicate recoveries and RPDs were within required control limits.

8. A matrix spike and a matrix spike duplicate were performed on samples 233854-3 (61BSD0010001) and 233854-8 (61ASD0030001). All matrix spike and matrix spike duplicate recoveries and RPDs were within required control limits.

9. All initial and continuing standard calibrations associated with these samples were within method control limits on the primary column. All SSV recoveries were within limits of 85%-115%.

10. Target compounds were not detected in the primary analysis. Therefore, a second column confirmation was not required.

=> 11. All manual integrations were performed following the laboratory's Manual Integration SOP and the reason for the manual integration is documented and reviewed. All manual integrations are identified as M1 (missed peak), M2 (mis-identified peak), M3 (poor baseline), M4 (peak not integrated correctly by data system) or M5 (other). Manual integration was not required for any ICAL standards, CCVs, samples, or QC samples associated with this SDG

Patti Gibson
Organics Section Manager

2/14/05
Date

Approvals and Signatures

Senior Vice President & Chief Operating Officer:	Dr. Keith C. Wheatstone	Date: 9/20/2004
Vice President, Client and Operations Services:	Dr. Charles W. Carter	Date: 9/20/2004
Corporate Quality Director:	Raymond J. Frederici	Date: 9/20/2004

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1.0 PURPOSE

This document describes STL's policy for proper manual peak integrations and requirements for documentation and review of manual peak integrations performed during the course of analyses.

2.0 SCOPE

This policy shall be enforced and followed throughout the laboratory. It applies to all STL laboratories for any analytical procedure involving identification or quantitation based on peak

analysis (e.g., GC, GC/MS, HPLC, IC). Each laboratory may have supplemental manual integration procedures or an addendum to this policy that describes additional details necessary to implement and enforce this policy. Any supplemental procedure or addendum must adhere to the requirements set forth in this policy.

3.0 POLICY

3.1 Supervisors must ensure proper training to all analysts and data reviewers using peak integration techniques. Analysts and data reviewers using peak integration techniques must be familiar with this policy and the applicable data processing system. This is to ensure that integration parameters are used in a manner that minimizes the need for manual integrations and that circumstances requiring manual integrations are performed in accordance with acceptable practices, documented and reviewed by a peer or supervisor. Audit trails or tracking systems MUST BE activated when the chromatographic system has this feature.

3.2 In some situations, manual integrations are necessary to compensate for imperfect chromatography, but manual integration must be performed ONLY when necessary. Baseline upsets, coelution and peak shape variation can sometimes complicate automatic integration and analyst intervention through manual integration may be required to assure consistency between area assignment for standards and samples.

3.3 Proper consistent manual integration is a critical quality control requirement. Appropriate manual integration is integration that can be technically justified. Manual integrations shall not be used to manipulate analytical results in order to meet method- or project-specific quality control (QC) acceptance criteria. Integration below the baseline is never appropriate. Inappropriate and inconsistent chromatographic peak integration to meet quality requirements is never allowed, nor is it to be used as a substitute for corrective action on the chromatographic system. Willful failure to follow this policy shall result in disciplinary action, up to and including termination.

3.4 The same integration technique must be applied **consistently** to any chromatogram i.e., field samples, calibration standards, calibration verification standards, and other applicable QC, etc., within the same analytical batch affected by the manual integration. Consistency in integration between standards and samples is one of the most important considerations in quantitative chromatographic analysis. Examples of appropriate and improper integration can be found in Appendix I and II.

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4.0 REASONS TO MANUALLY INTEGRATE

4.1 Undetected Peak

Routine mass spectrometer instrument tuning or the analysis of highly contaminated samples sometimes causes the relative abundances of ions of compounds present to deviate from reference criteria causing a peak to go undetected by the data system. A slight shift in chromatographic retention times can result in undetected peaks or false positive identification of compounds. If sample surrogate(s) retention times (RTs) shift, sample peaks need to be reviewed to ensure proper peak identification.

4.2 Incorrect Peak Integration

- Peak has small amount of splitting and the whole peak area was not integrated.
- Peaks close in retention times utilizing the same quantitation ions often integrate together as one peak, for example: ethylbenzene, xylenes; dichlorobenzenes, benzo(b)fluoranthene and benzo(k)fluoranthene.

4.3 Baseline Correction

- Matrix interferences caused by contaminated samples may interfere with calibrated compounds.

4.4 Other Examples of Events Requiring Manual Integration

- Incorrectly identified peak, where the wrong peak is chosen by the data system. This can occur both with the primary and the secondary ions.
- To remove a shoulder from a peak or to integrate a peak that only appears as a shoulder.

5.1 DATA SYSTEM PROCEDURES

5.1 The chromatography system's method integration parameters must be optimized to the greatest extent possible so compounds are properly identified and integrated with minimal operator intervention. (Note: even when integration parameters work properly for calibration standards, the analyst must ensure the integration is appropriate on all samples. The analyst must not assume that the chromatography system will automatically apply the correct integration). When manual integrations are necessary to identify peaks as targets (determine the RT), the calibration standards must be reprocessed after updating the retention times to demonstrate that the data system integration parameters are set properly. The following steps are required:

5.1.1 Process the file using the current data system parameters for the mid-level standard.

5.1.2 Identify all of the target compounds and assign the correct RT to each target. Manual integrations at this point do not have to be documented and must not be included in the calibration evaluation.

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5.1.3 Reprocess the data and confirm that all of the targets can be identified and properly integrated. If the targets cannot be identified and properly integrated, adjust the integration parameters and reprocess the data. This is an important step. If the data system cannot reliably detect and integrate the targets in the mid-level standard, the probability of properly identifying and quantifying the targets in the remaining standards and samples are low.

5.1.4 Process the remaining calibration standards and confirm that the data system can routinely and properly identify the target compounds at each calibration level. Pay particular attention to the lowest level standard because this standard typically defines the reporting limit (RL). The integration parameters should allow for detection of the target compounds down to the quantitation limit or reporting limit.

5.1.5 The integration parameters set at the initial calibration must remain in use until the next calibration is performed, except as noted in 4.3. Manual integrations are used only when the conditions listed in Section 3.0 are encountered. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system.

5.1.6 Any manual integration of a chromatographic peak or group of peaks must be documented. In all instances where the data system report has been edited or where manual integration has been performed, the chromatographic system operator must clearly identify such edits or manual procedures as listed below:

- Manual integrations indicated on expanded scale "after" chromatograms.
- Re-integration technique marked, if available, on the data system
- Technical justification for manual integration.
- Analyst's initials and date. (data system application of analyst name or initials is acceptable so long as the data system allows the analyst to log in as himself or herself and has password control)

5.1.7 Project specific, client, program or STL laboratory specific requirements for manual integration may exceed the requirements of this policy. In those instances, the more specific requirements will apply or written approval allowing a deviation from the requirement must be received. For example:

- Requiring the before and after printing of the chromatograms
- Handwritten or electronic initialing and dating the changes made to the report
- Hardcopy printout of the EICP of the quantitation ion displaying the manual integration included in the raw data for all standards and samples, this applies to internal standards and surrogates as well.
- Requiring manual integrations to be documented in the project or case narrative

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5.2 Data reviewers shall confirm that documentation of manual integration is complete and that each manual integration is appropriate. This inspection shall be documented. At a minimum, the information required in Section 5.1.6 must be reviewed.

5.3 If integration indicates problems with analytical instrumentation, investigate the problem and take action to correct it. If poor chromatography routinely interferes with the ability to identify and quantify components; is a result of delayed system maintenance; and is not inherent in the system, such as (benzoic acid for Method 8270; benzo(b)anthracene and benzo(k)anthracene merging with column age; and dichlorobutenes merging with column age), then instrument maintenance must be performed. If instrument and data conditions have changed such that the default integration parameters no longer work as effectively, it is acceptable to change the default parameters and reprocess all affected data, including the associated standards, lab QC, and field samples, using the new integration parameters. Further manual manipulations after this reprocessing must be treated as manual integrations. The reason for reprocessing must be documented and approved.

5.4 Manual integrations on some data systems (e.g., Multichrom) may consist of adjusting integration parameters on a by-sample basis. Changes such as these must be documented.

5.5 Any deficiencies must be resolved with the analyst or their supervisor before the results are approved and released from the analytical department. Any questions arising from review of the documentation must be investigated in the electronic record, when available, prior to data acceptance. Any failures to complete these requirements shall be described in a non-conformance report.

5.6 Any concerns about violations of this policy must be reported to the facility Quality Manager, Laboratory Director or the Corporate Quality Director.

5.7 Electronic data surveillance is performed using *Mint Miner*™ Software. This software allows the user to connect to a workstation or archived data source and evaluate the audit trails in the electronic data file (refer to WI-STL-002/A-08/03).

6.0 DEFINITIONS

- Integration: The determination of the area or height under a curve (peak).

- Manual integrations: Include any adjustments to measurements of analytical peaks not applied equally to all applicable samples and QC parameters in an analytical batch by the data acquisition system. For the purpose of this policy, a manual integration has been performed if results for any of the analyses could not be duplicated by another analyst using the indicated calibration and standard peak integration protocol. Manual adjustments to peaks can include baseline changes, retention time window adjustments, changes to peak identification in samples (calibration standards' changes as required are exempt), manual peak height measurements, or changes to the formula used to

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model analytical peak areas or changes to background subtraction algorithms for GC/MS tuning. Although the latest analytical instruments are equipped to perform automatic integrations, manual integrations are sometimes necessary to accurately analyze samples if peaks are poorly resolved, exhibit tailing, the baseline drifts or is noisy, or other similar situations.

- Chromatograms: In the context of this policy, chromatograms are not necessarily limited to the output of chromatography instruments or automated data systems. They can include strip charts, integrator printouts, computer screen dumps, or any graphic display of a continuous signal from an analytical detector.

- Chromatography: A separation technique involving differential retention of components between stationary and mobile phases.

- Baseline: The chromatographic signal plotted as a function of time in the absence of signal construction from components of interest.

- Peak: An increase in signal from baseline to a maximum and then back to baseline.

- Coelution: the concurrent elution of two or more compounds to the detector at the same time.

- Elution: The process of movement of compounds from the chromatographic system.

- "Wavy" Baselines: A "wavy" baseline can be caused by minor impurities in carrier gas or solvent.

- Negative Spikes: Negative spikes in chromatograms are sudden upsets in chromatographic signal below the normal baseline.

- Sudden Rise in Baseline: A rise in the baseline is caused by several factors including high concentration of components in the sample and by normal column bleed.

- Carry-over: Carry over results from system contamination from previous analyses and results in signal unrelated to the current analysis.

- Peak Tailing: Peak tailing is a delayed return of a peak to chromatographic baseline and could be related to a delay of compound elution from the chromatographic system by adsorption or dead volume effects.

- Interference Peaks or Fused Peaks: Peaks that partially or totally coelute with the peak of interest.

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7.0 APPENDICES

- Appendix I. Examples of Peak shape and Proper integration Documenting Manual Integrations
- Appendix II. Examples of Improper Integration and Inflection Point Guidance

8.0 TRAINING MODULE

- Acceptable Manual Integration Practices, September 2004, Version 1.1: T-Q-004.

9.0 REVISION HISTORY

- Revision 1; dated 12/1/01
- Revision 2; Amended Section 5.7; dated 9/17/04.

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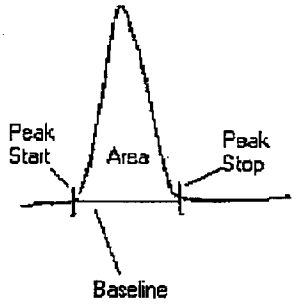
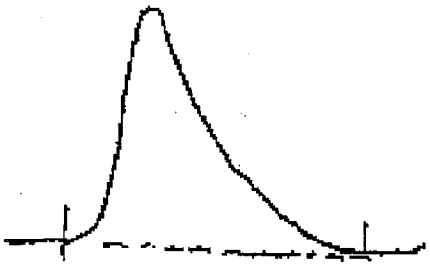
Appendix I.

Examples of Peak shape and Proper integration Documenting Manual Integrations

Ideal peak (Gaussian Shape) The start of integration is where the peak begins to rise from the background, and the end is where the peak returns to background.	
Tailing Peak Tailing peaks result from surface adsorption effects or dead volume in the instrument. When integrating tailing peaks, include only and all area that can be attributed to compound. If the baseline rises, the integration line should rise with the baseline.	

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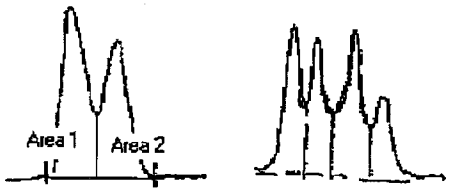
Fronting Peak Fronting peaks generally result from column overload and/or overcapacity. An example is benzoic acid on a 5% phenyl phase. In some cases, it is inherent in the analysis, in others, it is indicative of problems in the system. The analyst must have knowledge of their system. To integrate these peaks, it is important to have prior knowledge of how the compound acts when overloading versus co-eluting with a contaminate peak.	
Fused Peaks Fused peaks are near coeluters with some separation. They will occur in calibration mixes as well as real samples. To integrate, split the components with a vertical drop from the valley to the baseline.	
Hydrocarbon Envelope For semivolatile hydrocarbon analysis, most fuels produce "humpograms" like this one. Integration shall be performed in accordance with method, program or client specific requirements.	
Peak on a Baseline Rise Aside from hydrocarbon analysis, which uses the total area within a window for quantitation, baseline variations are not integrated. Therefore, skim the baseline rise to integrate the peak properly.	

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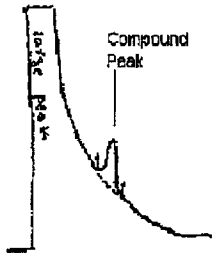
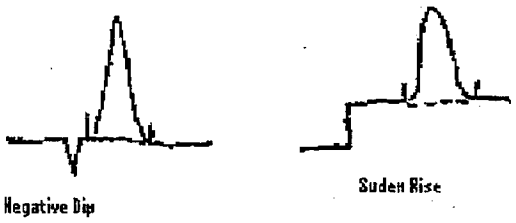
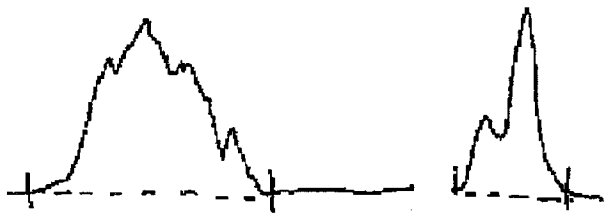
Skimmed Peak Use the tangent skimming functions of the integration software to correctly integrate small peaks on the tails of big peaks. Dropping vertical integration lines to the baseline of the big peak adds extra area which is not a part of the small peak, and results in high bias.	
Peak near a baseline upset Negative dips are common in ECD analysis, and the sudden rises in baseline are common with programmable fluorescence detectors where gain/wavelength switching occurs. Often, the default integration will go from the base of the negative peak to the far side of the peak of interest. This is results in high bias and is incorrect. Similarly, a default integration using the low part of the baseline rise and the far side of the peak of interest will also result in high bias and must be corrected.	
Split Peak Particularly in GC/MS analysis, low-level peaks may appear jagged or split. To integrate these properly, the analyst must have prior knowledge of the peak/compound chromatography.	

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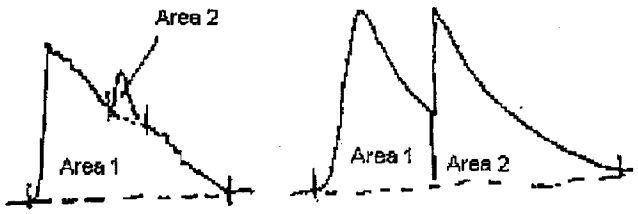
Fused tailing peaks These are very difficult to accurately quantify. It is best to do maintenance on the chromatography system to avoid this situation. To integrate these properly, the analyst should have prior knowledge of the compounds of interest. It is important to be consistent when integrating standards and samples.	

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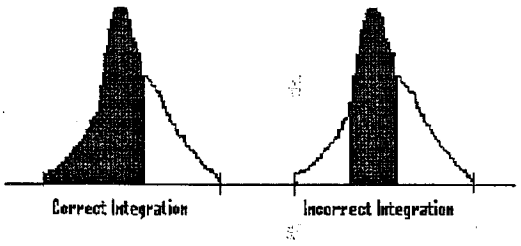
Appendix II.

Examples of Improper Integration and Inflection Point Guidance

An inflection point must be apparent when and if an integration point is drawn. For example:



When MS data has an inflection point in a peak, as shown in the example above, checking the underlying spectrum may be necessary to correctly manually integrate. On some chromatographic columns, for example, allyl chloride and carbon disulfide elute very close to each other, and they both share the primary characteristic ion mass 76. For both compounds mass 76 is the quantification mass. If two compounds can not be separated and a fused peak is going to be split at the inflection point, this can be correctly verified by looking at the spectra for each scan. In this example, the 76 peak may be fused, but the secondary ions will indicate which compound is present (carbon disulfide with secondary ion 78 and allyl chloride with secondary ions 41, 39 and 78).

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Attachment 6.

Requirements for DoD QSM Version 3.0

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DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Organics (GC/HPLC)

QC Check	Definition	Purpose	Evaluation
Breakdown Check 8081A: Endrin, DDT 8270C: DDT	Analysis of s standard solution containing Endrin and DDT. Area counts of these compounds and their breakdown products are evaluated to assess instrument conditions.	To verify the inertness of the injection port because DDT and Endrin are easily degraded in the injection port.	If degredation of either DDT or Endrin exceeds method-specified criteria, corrective action must be taken before proceeding with calibration
Confirmation of positive results (organics only)	Use of alternative analytical techniques (another method, dissimilar column, or different detector such as MS detector) to validate the presence of target analytes identified	To verify the identification of an analyte	This is a required QC procedure. All positive results must be confirmed.
CCV	This verification of the initial calibration that is required during the course of analysis at periodic intervals. Continuing calibration applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models	To verify that instrument response is reliable, and has not changed significantly from the current ICAL	If the values for the analytes are outside the acceptance criteria, the initial calibration may not be stable. Results associated with out-of-control CCV results require reanalysis or flagging
Demonstrate Acceptable Analyst Capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision	To establish the analysts' ability to produce data of acceptable accuracy and precision	The average recovery and standard deviation of the replicate must be within designated acceptance criteria.
Duplicate Sample	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are taken and prepared and analyzed identically.	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intralaboratory analytical process for a specific sample matrix	To provide information on the heterogeneity of the sample matrix. The greater the heterogeneity of the matrix, the greater the RPD between the sample and the duplicate
ICAL	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method	To establish a calibration curve for the quantification of the analytes of interest	Statistical procedures are used to determine the relationship between the signal response and the known concentration of analytes of int The ICAL must be successful be any samples or other QC check samples can be analyzed.
Internal Standards	A known amount of standard added to all standards and samples as a reference for evaluating and controlling the precision and bias of the applied analytical method	To verify that the analytical system is in control	Any sample associated with out-of-control results must be reanalyzed.
LCS containing all analytes required to be reported	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern.	To evaluate method performance by assessing the ability of the lab/analyst to successfully recover the target analytes from a control (clean) matrix.	This is a required QC Check. The inability to achieve acceptable recoveries in the LCS indicate problems with the accuracy/bias of the measurement system.
MS	A sample prepared by adding a know amount of targeted analyte(s) to an aliquot of a specific environmental sample	To assess the performance of the method as applied to a particular matrix	The lack of acceptable recoveries in the matrix spike often points to problems with the sample matrix. One test of this is a comparison to the LCS recoveries. If the corresponding LCS recoveries are within acceptable limits, a matrix effect is likely. The lab should not correct for recovery; only report the results of the analyses and the associated MS results and indicate that the results from these analyses have increased uncertainty
MSD	A 2nd replicate MS prepared in the lab, spiked with an identical, known amount of targeted analyte(s), and analyzed to obtain a measure of the precision of the recovery for each analyte	To assess the performance of the method as applied to a particular matrix and provide information of the homogeneity of the matrix.	When compared to the MS, the MSD will provide information on the heterogeneity of the sample matrix.

Table B-1 Cont.			
QC Check	**Definition**	**Purpose**	**Evaluation**
MDL Verification Check	A low-level spike taken through the prep and analytical steps at approximately 2x the MDL used to verify that the laboratory can detect analytes at the calculated MDL	To validate the MDL on an ongoing basis	If the MDL verification check fails, reprep/reanalyze at a higher level to set a higher MDL or the MDL study must be repeated.
MB	A sample of a matrix similar to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results.	To assess background interferences or contamination in the analytical system that might lead to high bias or false positive data.	This QC is used to measure lab accuracy/bias. The MB could indicate whether contamination is occurring during sample prep and analysis. If analytes are detected > ½ RL, reanalyze or B-Flag results for all samples in prep batch. For common lab contaminants, no analytes detected > RL. See DoD Box D-5; & Sec. D.1.1.1
MDL Study	The process to determine the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.	MDLs must be established prior to sample analysis. The RL or LOQ is at least 3x the MDL. Used in combination with the MDL verification check to validate the MDL on an ongoing basis.
RT window position establishment for each analyte (chromatographic methods only)	Determination of the placement of the RT window (start/stop time) of each analyte or group of analytes as it elutes through the chromatographic column so that analyte identification can be made during sample analysis. This is done during the initial calibration	To idendify analytes of interest	Incorrect window position may result in false negatives, require additional manual integrations, and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified.
RT window verification for each analyte (chromatographic methods only)	A standard is used to verify that the width and position of the RT windows are valid so that accurate analyte identification can be made during sample analysis	To minimize the occurance of both false positive and false negative results at each calibration verification.	The peaks from the standard used are compared to the RT window established during the ICAL to verify that the analytes of interest still fall within the window.
RT window width calculate for each analyte and surrogate (non-MS chromatographic methods only)	Determine the length of time between the sample injection and the appearance of a peak at the detector. The total length of time (window) is established for each analyte or groups of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.	To ensure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the standards and sample matrix to be analyzed. It is done to minimize the occurrence of both false positive and false negative results	Used to evaluate continued system performance. Tight RT windows may result in false negatives and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide RT windows may result in false positive results that cannot be confirmed upon further analysis.
Second source calibration verification	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration	The concentration of the 2nd source calibration verification, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. This independent verification of the ICAL must be acceptable before sample analysis can begin.
Surrogate spike (organic analysis only)	A pure substance with properties that mimic the analyte of interest. Surrogates are compounds unlikely to be found in environmental samples to evaluate analytical efficiency by measuring their % Recovery.	To assess the ability of the method to successfully recover specific non-target analytes from an actual matrix.	Whereas the MS is normally done on a batch-specific basis, the surrogate spike is done on a sample-specific basis. Taken with the information derived from other spikes (LCS; MS), the bias in the analytical system can be determined.

Notes:

1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

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DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-2: Organic Analysis by GC and HPLC - Methods 8015; 8081; 8082; 8141; 8151; 8310; 8330

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
IDOC	Per Instrument/Analyst	DoD acceptance criteria if available; otherwise method specific criteria	Correct / Repeat for those analytes which failed criteria	NA
MDL	Annually or quarterly MDL Checks performed	40 CFR 136B; MDL verification checks must produce a signal at least 3x the instrument's noise level.	Run MDL check at higher level and set MDL higher or reconduct MDL study	NA
RT window	At method set-up and after major instrument maintenance	RT width is ± 3x standard deviation for each analyte RT from 72-hour study	NA	NA
Breakdown check (Endrin/DDT-8081 only)	Daily prior to analysis of samples	Degradation ≤ 15% for both Endrin & DDT	Correct problem then repeat breakdown check	NA
ICAL	Initial 5-point calibration prior to sample analysis	One of the options below (Except for 8082. which may only use Option 1 or 2) **Option 1:** RSD for each analyte ≤ 20% **Option 2:** linear least squares regression: r ≥ 0.995 **Option 3:** non-linear regression: Coefficient of determination (COD) $r^2 \geq 0.99$ (6 points shall be used for 2nd order, 7 points shall be used for 3rd order)	Correct problem then repeat initial calibration	NA
2nd Source calibration verification	Once after each initial calibration	Value of 2nd source for all analytes within ± 20% of expected value	Correct problem and verify 2nd source standard. Rerun, if that fails, correct problem and repeat initial calibration.	NA
RT window position establishement for each analyte	Once per ICAL and at the beginning of the analytical shift	Position shall be set using midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift	NA	NA
RT window verification for each analyte & surrogate	Each calibration verification standard	Analyte within established window	Correct problem, then reanalyze all samples analyzed since the last acceptable RT check. If they fail, repeat ICAl and reset RT window	ICAL – NA CCV – apply Q-flag results for analytes outside of RT window
Calibration verification (ICV) and continuing (CCV)	ICV – Daily, before sample analysis CCV – After every 10 field samples and at end of analysis sequence. (DoD Box 58: CCV standards shall be at or below the middle of the calibration range)	All analytes within +/- 20% of expected value from ICAL (Data associated with an unacceptable CCV may be fully usable under the following conditions: 1. CCV (high bias) and samples ND, then raw data may be reported with appropriate flag 2. 2. CCV (low bias) and samples exceed maximum regulatory limit/decision level (DoD Box 60: Project specific permission from appropriate DoD personnel is required to report data generated from a run with noncompliant CCV.)	ICV – Correct problem, rerun ICV, if fails, repeat ICAL CCV – Correct problem, repeat CCV and reanalyze all samples since the last good CCV (DoD Box 59...if the lab chooses to demonstrate the success of routine corrective action through the use of 2 consecutive CCVs, then the concentrations of the two CCVs must be a two different levels within the original calibration curve with at least one falling below the middle of the calibration range.)	ICV – NA CCV – apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable CCV, if reanalysis is not possible
MB	One per prep batch	No analytes detected > ½ RL For common lab contaminants, no analytes ≥ RL	Correct problem, then see criteria in box D-5; if required, reprep/reanalyze MB and all associated samples	Apply B-flag to all results for the contaminated analyte for all samples in the associated prep batch
LCS (containing all analytes to be reported)	One LCS per prep batch	DoD specified QC criteria, if available	Correct problem, reprep/reanalyze the LCS and all samples in the associated prep batch for all failed analytes, if sufficient sample is available	Apply Q-flag to specific analyte(s) in all samples in the prep batch.
MS	One per prep batch per matrix	For matrix evaluation, use DoD specified QC criteria for LCS	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample
MSD or Sample Duplicate	One per prep batch per matrix	RPD ≤ 30% (between MS and MSD or sample and sample duplicate)	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample

Table B-2 cont.				
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
Surrogate	All field and QC samples	DoD specified QC criteria if available, otherwise method specific criteria or lab's own in-house criteria	For QC and field samples, correct problem, reprep/reanalyze all failed samples in the associated prep batch if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary	Apply J-flag for specific analyte(s) in all field samples collected from the same site matrix as the parent. Apply Q-flag to QC samples for specific analyte(s)
Confirmation of Positive Results	All positive results must be confirmed (exceptions: 8081A, toxaphene & technical chlordane 8015B, GRO, DRO	Calibration and QC criteria same for initial or primary column analysis. Results between primary and secondary column RPD $\leq$ 40%	NA Note: Report the higher of the two confirmed results unless overlapping peaks are causing erroneously high results – document in case narrative	Apply J-flag if RPD > 40% or Q-flag if sample is not confirmed. Discuss in the case narrative
Results reported between LOD and LOQ			Apply J-flag to all results between LOD (MDL) and LOQ (RL)	
Manual Integration	When manual integrations are performed	Raw data shall include a complete audit trail for those manipulations, raw data output showing the results of the MI (i.e., chromatograms of manually integrated peaks), and notation of rationale, date, and signature/initials of person performing manual operation.		Apply M-flag to MI data

Notes:
1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

SOP No.	Revision No.	Date	Page
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TITLE: HIGH PERFORMANCE LIQUID CHROMATOGRAPHY Nitroaromatics and Nitramines by SW-846 8330/8332

Updated by:	Signature:	Date:
Sharon A. Werner HPLC Chemist	Sharon A Werner	4.21.06

Approved by:	Signature:	Date:
Patti J. Gibson Section Manager, Organics Dept.	Patti Gibson	4-21-06
David W. Mazur Env. Health & Safety Coor.	D W Mz	4/21/06
Terese A. Preston Quality Manager	Terese A. Preston	4/20/06

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) outlines the trace analysis of explosive residues by High Performance Liquid Chromatography (HPLC) using a UV detector. This SOP was written using SW-846 Methods 8330, 8332, and 8000B as references and is used to determine the concentration of the following compounds in a water, soil, and sediment matrix.

ID	Compound	CAS No.*
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	2691-41-0
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine	121-82-4
1,3,5-TNB	1,3,5-Trinitrobenzene	99-35-4
1,3-DNB	1,3-Dinitrobenzene	99-65-0
Tetryl	Methyl-2,4,6-trinitrophenylnitramine	479-45-8
NB	Nitrobenzene	98-95-3
2,4,6-TNT	2,4,6-Trinitrotoluene	118-96-7
2,6-DNT	2,6-Dinitrotoluene	606-20-2
2,4-DNT	2,4-Dinitrotoluene	121-14-2
2-Am-DNT	2-Amino-4,6-dinitrotoluene	355-72-78-2
4-AM-DNT	4-Amino-2,6-dinitrotoluene	1946-51-0
2-NT	2-Nitrotoluene	88-72-2
4-NT	4-Nitrotoluene	99-99-0
3-NT	3-Nitrotoluene	99-08-1
NG	Nitroglycerine **	55-63-0
PETN	Pentaerythritol tetranitrate **	78-11-5

* Chemical Abstracts Service Registry Number
** Extraction and analysis are the same for these compounds, with the exception of the wavelength used for this analysis (sec.4.2.2)

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP) and authorized via laboratory signature approval; and amended to the data packages case narrative.

Specific requirements pertaining to the DoD QSM Version 3.0 are located in Attachment 7. These requirements are additionally applicable to all NFESC projects. Any deviations from these procedures and/or variance from must be addressed appropriately in accordance with standard operating protocols and pre-approved on a project by project basis.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Reporting Limits

Reporting Limits (Attachment 1) are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported.

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.2 Summary of Method

This method provides instrument operating parameters for the detection of ppb levels of certain explosives in extracts of soil, sediment or water samples by HPLC.

All of the compounds listed above are either used in the manufacture of explosives or are the degradation products of compounds used for that purpose. For compounds other than these, or for other sample sources, the analyst must demonstrate the usefulness of the method by performing an MDL study, and collecting precision and accuracy data on actual samples.

1.2.1 Low-Level Water Method (Salting Out)

Aqueous samples of low concentration are prepared for analysis by a reverse salting-out extraction procedure with acetonitrile and sodium chloride.

1.2.2 High-Level Water Method (Option)

Direct injection of diluted and filtered water samples can be used for water samples of higher concentrations. (Reporting limits can be established).

1.2.3 Soil and Sediment Samples

Soil and sediment samples are extracted using acetonitrile in an ultrasonic bath.

1.2.4 Solid Phase Extraction (SPE)

Aqueous samples are prepared for analysis by passing sample through a solid-phase media and then eluted from media by using appropriate solvent.

2.0 INTERFERENCES

- Solvents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interference under the conditions of the analysis by running method blanks.
- All glassware/equipment used in the preparation of standards (volumetric flasks, pipettes, beakers, eppendorf tips are rinsed well with the appropriate solvent and allowed to dry before use. After completion of standard preparation, unused amounts of standards are properly disposed of, and all glassware/equipment rinsed well with the appropriate solvent. Rinse/excess solvent is properly collected and disposed of. These procedures should eliminate positive interferences from these sources.
- All glassware used must be scrupulously clean prior to use. All re-usable glassware must be washed following procedures described in the laboratory glassware cleaning SOP (UQA-009). All glassware must also be rinsed at least 3 times with the appropriate solvent.
- Tetryl decomposes rapidly in methanol/water solutions, as well as with heat. All samples expected to contain Tetryl should **not** be exposed to temperatures above room temperature and not above 10°C when diluted for injection. It is imperative that the automatic liquid samplers employed have the capability of being chilled to <10°C to minimize Tetryl degradation while standards and samples are awaiting analysis.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

- 2,4,6-TNT is the analyte most often detected in high concentrations in soil samples. Soil samples as high as 2% 2,4,6-TNT can be safely ground. Samples containing higher concentrations should **not** be ground. The project manager or client must provide information as to whether the samples are suspected to contain explosives at a level greater than 2%. Visual observation of soil samples taken from a site expected to contain explosives is also important. Lumps of material that have a chemical appearance should be suspect and not ground. Explosives are generally a very finely ground grayish-white material.

- Parts of the instrument can be hot. Care should be taken if the instrument needs to be adjusted internally.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetonitrile	Flammable Poison	40 ppm-TWA	Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

4.1 Supplies

- Disposable luer-lock filters - 0.20 um Teflon® filter
- Pipettes: 10-mL, 9-mL, 5-mL, 1-mL glass, volumetric, Class A
- Pasteur pipettes
- Disposable 10-mL syringe with Luer-Lock fitting
- 6x125mm screw-top (Teflon-lined) test tubes
- 1.5-mL amber autosampler vials
- Eppendorfs: 100 uL-1000 uL size (adjustable)
- Air-forced drying oven
- Volumetric flasks (glass, Class A): 5.0-mL and 10.0-mL
- 1.0 L Erlenmeyer flask
- 125-mL Erlenmeyer flask

- Magnetic stir bars
- Automatic magnetic stirrer
- Muffle furnace capable of 400°C
- Temperature-controlled ultrasonic bath
- Water chiller recirculator capable of achieving <10°C
- Balance, ± 0.1 mg
- Vortex, VWR, Vortex Genie 2, or equivalent
- Vacuum Pump
- Strata SPE Manifold

4.2 HPLC System

- 4 - Agilent 1100 HPLCs equipped with UV detectors and autosampler with a refrigerated water circulator capable of chilling extracts to <10°C.

4.2.1 HPLC Columns

- Primary Column: Phenomenex Ultracarb (C18), 5u ODS (20); 250 x 4.6mm ID
- Confirmation Column: Phenomenex Luna 3u Phenyl-Hexyl 150 x 4.6mm ID

4.2.2 HPLC Conditions

Primary Column	Secondary Column
Phenomenex Ultracarb (C18), 250 x 4.6 mm ID, 5 micron particle size, normal phase.	Phenomenex Luna Phenyl Hexyl, 150x4.6mm ID, 3 micron particle size, reverse phase
Mobile Phase: 50% water / 45% MeOH / 5% ACN*	Mobile Phase: 59% 0.1% H3Po4/ 41% 9:1 MeOH / ACN *
Flow Rate: 1.0 mL/min*	Flow Rate: 1.0 mL/min*
Injection volume: 100 uL*	Injection Volume: 100 uL*
UV Detector: 254 nm*/**	UV Detector: 254 nm*/**
Column Temperature: 30°C	Column Temp.: 35°C
Range 0.100 Au	Range: 0.200 Au

* Conditions may be varied to achieve optimum separation.
** When analyzing for NG and PETN a wavelength of 210 nm must be used for C18 column and a wavelength of 214 nm for the Phenyl Hexyl column.

4.2.3 Data Collection

Each HPLC uses TurboChrom for data acquisition and Target for processing data.

5.0 Reagents and Standards

5.1 Reagents

- Laboratory pure water (Milli-Q)
- Methanol (MeOH) - HPLC grade or better
- Acetonitrile (ACN) - HPLC grade or better

- Sodium Chloride, NaCl, Reagent grade. Kilned at 400°C for 4 hours. Stored in glass bottles.

5.2 Standards

Stock standards are purchased as solutions generally from Restek and Cerrilant. When available, standards with A2LA, CRADA or EPA certifications are purchased. If unavailable, the standards are verified against an alternate source.

These solutions are purchased at concentrations such that appropriate dilution's can be made to achieve desired concentrations. When making stock solutions for calibration, treat each explosive compound with caution.

The preparation of all standards and QC solutions must be properly documented. All standards and QC solutions must be labeled with the date of preparation, expiration date, analyst, and concentrations of analytes. Standards must be stored in glass containers with Teflon-lined lids at 4±2°C protected from the light. Stock standards must be replaced after 1 year or sooner if comparison with a check standard indicates a problem.

5.2.1 Parent Surrogate Solution: 20 ug/mL

The surrogate solution (1,2-Dinitrobenzene) is purchased from a vendor at a concentration of 1,000 ug/mL. The Parent Surrogate Solution is prepared by diluting 1-mL of surrogate with ACN to a final volume of 50-mL. This produces a final concentration of 20 ug/mL.

5.2.1.1 Working Surrogate Solution: 2 ug/mL

The Working Surrogate Solution is prepared by volumetrically diluting 10.0-mLs of the Parent Surrogate to 100.0-mLs of ACN (1/10 dilution), resulting in a concentration of 2.0-ug/mL. 600 uLs is added to water samples; and 1.0 mL is added to soil samples.

- Label Information: All standard labels must contain the date prepared, the date of expiration, the analyst name, and the standard number.
- Storage / Life: All standard and spikes must be stored in Teflon-sealed screw-capped bottles with minimal headspace at 4 ± 2°C and protected from light. This solution is valid for 30 days.

5.2. Laboratory Control Sample (LCS) and Matrix Spike (MS)/MS Duplicate (MSD)]

Two different explosive spike mixes are purchased from Cerrilant for the preparation of the working spike solution.

Mix #1	Mix #2
HMX	Tetryl
RDX	2,6-Dinitrotoluene
1,3,5-Trinitrobenzene	2-Nitrotoluene
1,3-Dinitrobenzene	3-Nitrotoluene
Nitrobenzene	4-Nitrotoluene
TNT	2-Amino-4,6-DNT
2,4-Dinitrotoluene	4-Amino-2,6-DNT

Their concentrations are about 100-ug/mL. The Spike is prepared by adding 1.0-mLs of Mix #1 and 2.0-mLs of Mix #2; and brought up to a final volume of 50-mL in ACN. The final concentrations are 20 ug/mL (Mix #1) and 40 ug/mL (Mix #2). Independently, PETN and NG are prepared in the same manner using 1.0-mL of each to a final volume of 25-mL giving a final concentration of 40 ug/mL.

5.2.2.1 Working Spike Solution: 2.0 ug/mL / 4.0 ug/mL

The Working Spike Solution is prepared by diluting 1.0 mL of the Parent Spike Solution to 10.0 mLs ACN (1/10 dilution). The final concentrations are 2.0 / 4.0 ug/mL (Attachment 2). 600 uLs are added to water samples and 1 mL is added to soil samples.

- Label Information: All standard labels must contain the date prepared, the date of expiration, the analyst name, and the standard number.
- Storage / Life: All standard and spikes must be stored in Teflon-sealed screw-capped bottles with minimal headspace at 4±2°C and protected from light. This solution is valid for 30 days.

5.2.3 Parent Calibration Standards

Calibration standards are prepared in ACN. One of the concentration levels should be at, or below a concentration equivalent to the reporting limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the HPLC. Explosive standards are purchased individually from a vendor for the preparation of the intermediate solutions Mix #1 and Mix #2.

Mix #1	Mix #2
HMX	Tetryl
RDX	2,6-Dinitrotoluene
1,3,5-Trinitrobenzene	2-Nitrotoluene
1,3-Dinitrobenzene	3-Nitrotoluene
Nitrobenzene	4-Nitrotoluene
TNT	2-Amino-4,6-DNT
2,4-DNT	4-Amino-2,6-DNT

Their concentrations are 100 ug/mL. The Parent standard is prepared by adding 0.5-mL of Mix #1, 1.0-mL of Mix #2, and 0.5-mL of the surrogate. Dilute to a final volume of 50-mL in ACN. The resulting concentrations are listed in Attachment 2. NG and PETN are made independently using 1.0-mL of each and 0.5-mL of the surrogate to a final volume of 50-mL in ACN.

- Label Information: All standard labels must contain the date prepared, the date of expiration, the analyst name, and the standard number.
- Storage / Life: All standard and spikes must be stored in Teflon-sealed screw-capped bottles with minimal headspace at 4±2°C and protected from light. This solution is valid for 30 days.

5.2.3.1 Working Calibration Standards

6-concentration levels are prepared through dilution of the Parent Calibration Standard and are prepared fresh on the day of calibration. The resulting calibration range in relative concentrations ranges from 0.02/0.04 ng/uL through 1.0/2.0 ng/uL. Refer to Attachment 2 for a listing of the concentrations.

- Label Information: All standard labels must contain the date prepared, the date of expiration, the analyst name, and the standard number.
- Storage / Life: All standard and spikes must be stored in Teflon-sealed screw-capped bottles with minimal headspace at 4±2°C and protected from light. This solution is valid for 30 days.

5.2.4 Continuing Calibration Verification (CCV)

The CCVs are alternating mid-level standards; and the concentrations are consistent with the cited Levels 4 and 5 concentrations listed in Attachment 2.

- Label Information: All standard labels must contain the date prepared, the date of expiration, the analyst name, and the standard number.
- Storage / Life: All standard and spikes must be stored in Teflon-sealed screw-capped bottles with minimal headspace at 4±2°C and protected from light. This solution is valid for 6 mos.

5.2.5 Second Source Verification (SSV)

The SSV is second-source standard consistent with the Level 5 concentration listed in Attachment 2. (Some clients request the SSV at the Level 2 concentration).

- Label Information: All standard labels must contain the date prepared, the date of expiration, the analyst name, and the standard number.
- Storage / Life: All standard and spikes must be stored in Teflon-sealed screw-capped bottles with minimal headspace at 4±2°C and protected from light. This solution is valid for 6 mos.

6.0 CALIBRATION (NON-DAILY)

Explosives are confirmed by use of a second column (Section 4.2.2). The acceptance criteria for this analysis is identical to that of the primary column.

6.1 Retention Time Windows

Before establishing retention time (RT) windows, make sure the HPLC system is within optimum operating conditions. Make 3-injections of a standard throughout the course of a 72-hour period. Serial injections over less than a 72-hour period may result in retention time windows that are too tight.

± 3X Standard Deviation of the absolute RTs for each standard will be used to define the RT window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

The laboratory must calculate RT windows for each analyte on each LC column and whenever a new LC column is installed. The data must be retained by the laboratory and available for review.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	< Reporting Limit
Lab Control Sample (LCS)	1 in 20 or fewer samples	Statistical control limits [4]
LCS Duplicate (LCD) [1]	1 in 20 or fewer samples	Statistical control limits
Matrix Spike (MS) [2]	1 in 20 or fewer samples	Statistical control limits
MS Duplicate (MSD) [2]	1 in 20 or fewer samples	Statistical control limits
Surrogate	every sample [3]	Statistical control limits

[1] LCDs are performed only when insufficient sample is available to perform the MS/MSD or when requested by the client/project/contract.

[2] If not designated, the sample selection for MS/MSD are rotated among client samples so that various matrix problems may be noted and/or addressed.
[3] Analytical and QC samples.
[4] Internal statistical control limits are updated; refer to Attachment 1.

7.2 Sample Preservation and Storage

Samples are to be collected in glass containers with Teflon-lined lids. All samples are to be maintained at 4±2°C, in the dark, prior to and after extraction/analysis.

Matrix	Holding Time (VTS): (to Extract)	Holding Time: (Extraction to Analysis)
Soil / Sediment	14 days	40 days
Water	7 days	40 days

VTS: Verified Time of Sampling

7.3 Sample Preparation

7.3.1 Reverse Salt-Out Extraction (Low - Level Waters)

7.3.1.1 Measure out 770 mL of sample (using a 1-liter graduate) and transfer it to a 1-liter narrow neck Erlenmeyer flask, or 1-liter volumetric flask. Add 251.3 g of NaCl (kilned at 400°C for 4 hours) to the sample. Add a stir bar and mix the contents at maximum speed on a magnetic stirrer until the salt is completely dissolved.

7.3.1.2 Using an adjustable microdispenser, add 600 uLs of working surrogate solution to each sample, MB, LCS, and MS/MSD. Add 600 uLs of working spike solution to the LCS and MS/MSD.

7.3.1.3 Continue the stirring motion and add 164 mLs HPLC grade ACN. Stir for 15 minutes. Allow the phases to separate for 10 minutes. Remove the top ACN layer (about 8 mLs) with a Pasteur pipette and transfer it to a 125 mL narrow neck Erlenmeyer flask, or a 100 mL volumetric flask.

7.3.1.4 Add 10 mLs of fresh ACN to the original sample and stir for 15 minutes. Allow the phases to separate for 10 minutes. Remove the top ACN layer and add to the Erlenmeyer containing the original ACN extract.

7.3.1.5 Add 84 mLs of saturated salt solution (325.1 g NaCl/1 L H_2O) to the 125 mL Erlenmeyer containing the ACN sample extract. Stir for 15 minutes. Allow to separate for 10 minutes.

7.3.1.6 Remove the top ACN layer and add it to a graduated test tube which accurately measures <10.0 mL. (It is imperative at this point to not allow the transfer of any saturated salt solution with the ACN.)

7.3.1.7 Add 1.0 mL fresh ACN to the Erlenmeyer and stir for 15 minutes. Allow to separate for 10 minutes. Remove the top ACN layer from the Erlenmeyer and add to the first extraction aliquot in the graduated test tube.

7.3.1.8 Adjust the final volume to 6 mLs. On occasion, the final volume ends up being greater than 6 mLs. Document the final volume appropriately.

7.3.1.9 Filter the extract through a 0.2 um Teflon filter prior to analysis.

7.3.1.10 All sample extracts and standards are diluted 1:1 with filtered Milli-Q water prior to analysis on the C18 column. All sample extracts and standards are diluted 1:2 with filtered Milli-Q water prior to analysis of the Phenyl Hexyl column.

7.3.2 High-Level Waters (Option)

Sample filtration: Place a 5 mL aliquot of each water sample in a 16x125mm test tube. Add 5 mLs of ACN, shake thoroughly, and filter through a 0.2 um Teflon filter using a disposable syringe. Discard the first 3 mLs of filtrate, and retain the remainder in a Teflon-capped vial for HPLC analysis.

7.3.3 Soil and Sediment Samples

7.3.3.1 Dry a homogenized, representative portion of each soil sample in an air-forced drying oven being careful not to expose the sample to direct light - soils/sediments are dried to a constant weight. Add the MB soil (Ottawa sand) into the oven along with the samples. This will ensure no cross contamination occurs during the drying process.

Pulverize the dried sample with a mortar and pestle. It is imperative that the mortar and pestle be rinsed thoroughly between samples to prevent the possibility of cross contamination. With a spatula, remove any sticks, rocks or other extraneous material. Particle size should resemble soil passed through a 30 mesh sieve.
NOTE: See safety section regarding extraction of wet soils for high level samples.

7.3.3.2 Weigh a 2.0 g aliquot of each dry, pulverized, soil sample into a properly labeled, 16x125mm screw-top test tube. Add 1.0 mL of working surrogate solution to each sample, MB, LCS, and MS/MSD. Add 1.0 mL of working spike solution to each sample, LCS, and MS/MSD. Add ACN to achieve a final volume of 10.0 mLs. Cap with a Teflon-lined screw cap. Vortex each sample for 1 minute. Store the extra, pulverized sample in small, labeled vials for future use, if needed.

7.3.3.3 Place the test tubes (contained in a test tube rack) in an ultrasonic bath and extract for 18 hours.

7.3.3.4 To minimize Tetryl breakdown, the ultrasonic bath must be chilled to <10°C. This may be achieved by running a line from the water chiller recirculator into the bath to chill the bath to <10°C.

7.3.3.5 After sonication, centrifuge each sample tube to separate the soil from the extract. Place the supernatant in a disposable syringe and filter through a 0.2 micron Teflon-filter. Sample is then prepared for instrument as is Section 7.3.1.10

7.3.3.6 Solid Phase Extraction (SPE) Method 3535 (See Attachment 6).

7.4 Calibration / Standardization

Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument. Preparation of all reference materials used for calibration must be documented.

Calibration Controls	Sequence	Control Limit
Calibration Standards	5-point (minimum) curve	≤ 20% RSD
Cont. Cal. Verif. (CCV)	Prior to and after every 10 injections	±15% pred. response
RT Windows (RTW)	Initial CCV determines midpt. of RTW	± 3X SD

All standards and samples must be allowed to equilibrate in the autosampler chiller prior to analysis.

All electronic equipment is allowed to warm up for 30-minutes. During this period, at least 15 void volumes of mobile phase are passed through the column (~20 min at 1.5 mL/min) and continued until the baseline is level.

7.4.1 Instrument Calibration

7.4.1.1 Prepare a minimum of 5 levels of calibration standards (Attachment 2). The calibration standards define the working range of the HPLC with the lowest standard being at or below the reporting limit.

7.4.1.2 Inject each calibration standard using the same sample introduction technique that will be used to introduce the actual samples into the HPLC. The ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent standard deviation (%RSD) of the calibration factors is ≤ 20%, linearity through the origin can be assumed and the average response factor (RF) can be used for calculations. Alternatively, if a correlation coefficient of ≥0.995 is obtained, linear regression may be used for calculating compounds.

$$\text{Calibration Factor} = \frac{\text{Peak Area (or Height)}}{\text{Mass injected (nanograms)}}$$

$$\text{Response Factor (RF)} = \frac{\text{Concentration}}{\text{Peak Area (or Height)}}$$

7.4.1.3 The working calibration curve, or calibration factor, must be verified on each working day by injecting the alternating CCVs (mid-level standards). If the response for any analyte varies form the predicted response by more than ±15% Difference, a new calibration curve must be prepared for that analyte, unless maintenance can be performed which brings the instrument back into control.

7.4.1.4 Calibration Evaluation and Acceptance Criteria

Refer to the STL Corporate Procedure, P-T-001, 'Selection of Calibration Points' (Attachment 3) or on STLs Intranet.

7.5 Preventive Maintenance

- Laboratory pure water must be filtered, using an all-glass apparatus, through 0.2um filter prior to use on the instrument.
- If peak splitting occurs, an increase in pressure is usually seen. The source of the increase is most likely a plugged purge valve frit or pre-column filter. The column itself may be the source of increased pressure. This is easily checked by substitution with a known good column. As a last resort the column's internal frit may be changed. Care should be taken not to disturb the column's packing. Disturbance of the packing may result in voids within the column and channeling.

7.6 Sample Analysis

7.6.1 Samples are analyzed in a set referred to as an analytical sequence. This sequence begins with the analysis of a CCV. If comparison of the CF from the CCV are within ±15% difference of the average CF from the calibration curve, then the analysis sequence may proceed with a MB, followed by the LCS and then the samples. If the CF of the CCV is greater than ±15% difference, a new calibration sequence must be analyzed.

7.6.2 A CCV must be injected after every 10 injections. The CF for each analyte to be quantitated must not exceed a 15% difference when compared to the initial calibration sequence. When this criterion is exceeded, inspect the HPLC system to determine the cause and perform whatever maintenance is necessary before re-analyzing the standard. If the CF still exceeds the 15% difference criteria, a new calibration sequence is required. All samples must be bracketed by standards that are within control.

7.6.3 If the response of any sample exceeds the linear range of the system, dilute the sample and re-analyze.

7.6.4 Establish daily RT windows for each analyte. Use the absolute RT for each analyte from the beginning of the sequence as the midpoint of the window for that day. The daily RT window equals the midpoint ± 3X the standard deviation (Sec. 6.1).

7.6.5 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily RT window. Confirmation is required on a second HPLC column. When at sufficient concentrations, GC/MS confirmation may be used.

7.6.6 Validate the qualitative performance of the HPLC system by running the alternating mid-level CCVs throughout the analysis sequence to evaluate this criterion. If any of the standards fall outside their daily retention time window, the system is out-of-control. Determine the cause of the problem and correct it.

7.7 Manual Integration Policy

In each case where manual integrations have taken place, the operator must identify, initial and date the changes on the hardcopy. The following guidelines apply with further details available in STLs Corporate SOP for manual integrations (S-Q-004) located in Attachment 8. An example of one such integration and documentation is included in the attachment.

- Manual integrations should be consistent between all files integrated.
- Manual integrations should not be performed to meet QC criteria.
- Manual integrations are automatically flagged with an 'M' on the raw data.
- Excessive manual integrations may reflect an instrumental or methodological problem that should be addressed.

Manual integrations are most often performed for the following reasons:

- Assignment of correct peak that was mis-identified by the data system.
- Incomplete auto-integration due to high level of target compound detected.
- Incomplete auto-integration due to background interference.
- Incorrect auto-integration due to co-elution or near co-elution of compounds.
- Missed peaks.

All integrations are reviewed by the analyst. All chromatograms and reports are printed after any integration take place and are routinely included in the data packages. Manual integrations may be documented within the narrative (if so required), however, reference to this and the Corporate Manual Integration SOP will be used for explanations and any further documentation beyond initials and dates will not be done.

7.8 DOCUMENTATION

7.8.1 Instrument Run Logs

The analysis of samples and standards is documented within each instrument-specific run log (Attachment 4), and must be completed for each day's analysis.

7.8.2 Traceability of Standards

Upon receipt or preparation, each standard is entered into LIMS and is issued a unique ID# based upon the type and sequential order in which the item was received. Further information entered into the database includes the manufacturer, lot #, the date received or prepared, the expiration date, volume/weight received; concentration; preparation details (if applicable), initials of the recording analyst, and the description of the item (i.e., **XXXX** Stock Solution – LCS/MS). Once the record is created, a unique label is printed and affixed to the appropriate standard bottle.

7.8.3 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews according to the criteria established on the data review checklist (Attachment 5). Upon the first 100% review, the checklist is initialed and dated as reviewed. The package, with its checklist, comments and any CARs, is submitted to the section manager or peer reviewer for a second review. Once again, the checklist is initialed and dated by the second reviewer. The completed data review checklist remains on file with the original data

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 At least one MB and LCS will be included in each laboratory lot of 20 or fewer samples. The MB will be examined to determine if contamination is being introduced in the laboratory. The MB and LCS must be carried through all stages of the sample preparation and measurement steps. The results of these are tabulated by the QA department to generate in-house control limits.

8.1.2 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

8.1.3 Precision will be measured by the reproducibility of the MSs and will be calculated as Relative Percent Difference (RPD). If MSs were not analyzed, reproducibility will be measured using the LCS/LCD. Results must agree within statistical control limits in order to be considered acceptable.

8.1.4 Surrogate compounds will be added to every analytical and QC sample to measure the performance of the analysis. Results must agree within statistical control limits in order to be considered acceptable.

8.1.5 Each time an analytical sequence is started, the standards must be evaluated to determine if the chromatographic system is operating properly. The analyst should consider--Do the peaks look normal?, is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatograms can indicate whether the column is still good, the injector is leaking, etc....

8.1.6 The laboratory must maintain records to document the quality of the data generated. When results of the LCS indicate irregular method performance, a quality control check standard should be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.7 Before analysis of any samples, the analyst should demonstrate, through the analysis of a MB that interference from the analytical system, glassware and reagents are under control.

8.1.8 If any changes are made to the chromatographic system, recalibration of the system must take place.

8.1.9 Required Instrument QC

- The method requires that the %RSD vary by <20% when comparing calibration factor to determine if a five (or more) point calibration is linear through the origin. If the %RSD is <20%, the average CF from the calibration can be used to quantitate the samples. Alternatively, linear regression can be used to quantitate the samples; however, a correlation coefficient of 0.995 should be achieved prior to using the curve.
- CCVs must be within ±15% difference from the average CF of the linearity. If the limit is exceeded, corrective action must be taken to correct the problem, or the sequence must be started over. All samples should be bracketed by acceptable CCVs and all analytical runs are closed-out with a CCV. There are situations where if samples are clean, and a CCV displays an increase in sensitivity, the samples don't have to be re-analyzed. This issue must be dealt with on a case-by-case situation and must be documented and approved prior to reporting any data.
- RT windows must be established.
- All continuing standards must fall within their daily RT windows.
- For every batch of samples (≤ 20 samples/batch), a MB, LCS, and MS/MSD must be performed. Also, every sample, MB, LCS, MS/MSD must be spiked with the surrogates.
- Limits used for spike recoveries are statistically generated limits, or limits which have been specifically requested by the client (refer to project QAP).

8.2 Corrective Action

When an out-of-control situation occurs, the analysts must use his/her best analytical judgment and available resources when determining the action to be taken. The out-of-control situation may or may not be caused by more than one problem. The analyst should seek the help of his/her supervisor, QA personnel, or other experienced staff if he/she are uncertain of the cause of the out-of-control situation and the corrective action. The analysis must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out-of-control situation must be reanalyzed. Out-of-control data must never be released without approval of the section manager, QA personnel, or the laboratory manager.

Listed below are steps that MUST be taken when an out-of-control situation occurs:

- demonstrate that all the problems creating the out-of-control situation were addressed,
- document the problem and the action which was taken to correct the problem on a corrective action report (CAR) form,
- document on the CAR that an in-control situation has been achieved; and
- receive approval (signature) of the section manager, QA personnel, or the laboratory manager prior to release of any analytical data associated with the problem.

NOTE: See your section manager if at any time the analyst is uncertain as to what actions to take or how to perform suggested maintenance; or if something unusual is happening that is not described in this section. Costly damage can result to the instrument, detector, or column if maintenance is not performed correctly.

8.2.1 Calibration Curve

- Reanalyze the standard curve.
- Prepare new stock and/or working standards.

8.2.2 Continuing Calibration Verification (CCV)

- Repeat CCV to verify proper preparation.
- Prepare new CCV from original stock.
- Check for instrument drift.
- Recalibrate with new standard curve and repeat all samples since the previous in-control CCV.
- Prepare new stock and/or working standards.

8.2.3 Laboratory Control Sample (LCS)

If the LCS is low

- Re-inject the extract to ensure the error wasn't an injection error.
- Determine the source of the error, re-extraction of the entire set may be necessary. Initiate a Sample Discrepancy Report (SDR) so the project manager or section manager can determine if re-extraction is required.

If the LCS is high

- Re-inject the extract to ensure the error wasn't an injection error.
- Check for source of possible contamination, re-extraction of the entire set may be necessary.
- Initiate an SDR so the project manager or section manager can determine if re-extraction is required. If all samples are non-detects, this situation may be able to be narrated.

8.2.4 Method Blank (MB)

The MB should not have any target compounds present above the reporting limit.

- Re-inject the MB to verify that the contamination is not within the chromatographic system.
- Determine the level of contamination in the MB and in the associated samples. If the associated samples are either non-detects, or have the same target compound as the MB at a level >10 times what was in the MB, the data may be acceptable to report.
- Initiate an SDR immediately, so that the project manager or section manager can determine if re-extraction is necessary.

8.2.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

- Re-inject the extracts to ensure the error wasn't with the injection.
- If both the MS/MSD are biased low, or both are biased high, and the RPD is within control, sample matrix may be assumed as the cause.
- Otherwise, initiate an SDR so that the appropriate actions can be taken. Re-extraction may be required.

8.2.6 Retention Time Windows

Initial RT windows must be established following the procedure described in Section 6. Daily windows are established (Section 7.6.4) at the beginning of each analytical sequence. If a continuing standard has any analytes that are outside of their daily windows, corrective actions must be taken before continuing.

- Evaluate the data for usability based on a comparison with the standards run during the analytical sequence.

- Consider the RTs for the surrogates and spiked compounds analyzed before and after the sample in question.
- Check the instrument for leaks, check flows, and pressures.
- Document using a CAR.

8.2.7 Surrogate Spike

The recoveries for the surrogate(s) should be within statistical control limits.

- Check calculations and spike preparation for documentable errors.
- If the surrogate recoveries in the MB and LCS are within the control limits, then sample matrix effects are the most likely cause. However, any samples with surrogate recoveries significantly below the control limits with, no visible chromatographic cause, should be reanalyzed to determine if an injection error was the cause for the low recovery.
- If the surrogate recoveries in the associated MB and LCS are not within control limits, and the samples are within the holding time, then re-extract all associated samples.
- If the samples are outside the holding time, then contact the project manager using and SDR.

Unless otherwise directed, samples will not be re-analyzed out of hold time and data will be submitted with appropriate narration.

8.2.8 Continuing Calibration Verification (CCV)

Alternating mid-level CCVs are run after every 10 sample injections. The response factors of the CCV should not vary from the average response factor of the initial calibration by more than ±15%. If any of the target compounds fail this criteria, then the standard is considered to be non-compliant.

- Re-analyze the standard.
- If the standard is still non-compliant, then prepare a new standard.
- If the new standard is non-compliant, then recalibrate the instrument with a new curve.
- Any samples bracketed by a standard that does not meet this criteria, must be reanalyzed.
- Notify the project manager of any non-compliance using the SDR.

Unless directed otherwise, samples will not be analyzed outside of holding time and the data will be submitted with appropriate narration.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Concentration (ppb) = $\frac{[(A_1)(A)(V_1)(D)]}{[(A_2)(V_i)(V_s)]}$

Where:
A_1 = response for the analyte in the sample (area or height)
A = amount of standard injected (ng)
A_2 = average CF for the linearity (area or height, which ever was used for A1)
V_i = volume of extract injected
D = dilution factor
V_t = volume of total extract (uL)
V_s = volume/weight of sample extracted.

9.2 %RSD = $\frac{\text{Standard Deviation}}{\text{Mean}} \times 100$

Where:

$$\text{Std. Dev.} = \frac{\left| \sum_{i=1}^{n} (x_i - \bar{x})^2 \right|^{1/2}}{n - 1}$$

Where:
x_i = each individual value used to calculate the mean
$\bar{x}$ = the mean of n values
n = the total number of values

9.3 % Difference = $\frac{\text{Avg. CF} - \text{CF}}{\text{Avg. CF}} \times 100$

Where:
Avg. CF = Average CF from initial linearity
CF = CF from the analysis of the verification standard

9.4 Surrogate % Recovery = $\frac{Q_d}{Q_a} \times 100$

Where:
Q_d = Quantity determined by analysis
Q_a = Quantity added to sample/blank

9.5 Spike %Recovery = $\frac{SR}{SA} \times 100$

Where:
SR = Spike Result
SA = Spike Added

9.6 Accuracy (%R) = $\frac{(A_T - A_O)}{A_F} \times 100$

Where:
A_T = Total amount recovered in the fortified sample
A_O = Amount recovered in the unfortified sample
A_F = Amount added to sample

9.7 Precision (RPD) = $\frac{|B_1 - B_2|}{(B_1 + B_2) / 2} \times 100$

Where:
B_1 = % Recovery MS (or LCS)
B_2 = % Recovery MSD (or LCD)

NOTE: All dry weight corrections are made in LIMS at the time the final report is prepared.

10.0 WASTE MANAGEMENT AND POLLUTION CONTROL

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Solid sample waste will be placed in the "Non-Hazardous" waste buckets.
- Acetonitrile/Methanol/Water mixture will be collected in approved containers and poured into the drum labeled "Flammable Solvent" waste using a funnel to reduce splashing.
- Expired and single component standards will be turned over to the EHSC or Waste Technician.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

Table 1. Retention Times

Attachment 1. Example: Reporting Limits, MDLs, and Statistical Control Limits
Attachment 2. Standards; Working Spike and Working Surrogate Concentrations
Attachment 3. STL Corporate Procedure, P-T-001, 'Selection of Calibration Points'
Attachment 4. Example: Analysis Run Log / Maintenance Log
Attachment 5. Example: Data Review Checklist
Attachment 6. Solid Phase Extraction (SPE) Method 3535
Attachment 7. DoD QSM Version 3.0 Requirement Tables
Attachment 8. STL Corporate Policy S-Q-004, 'Acceptable Manual Integration Practices'

Historical File:

Revision 00: 09/09/94
Revision 01: 09/28/94
Revision 02: 10/24/96
Revision 03: 06/17/97
Revision 04: 12/30/98
Revision 05: 05/14/99
Revision 06: 04/18/00
Revision 07: 03/28/02
Revision 08: 02/17/04
Revision 09: 03/30/05
Revision 10: 04/21/06

Revision 10; Reasons for Change:

- Annual Review
- Section 5.2.1.1 updated how dilution is made
- Section 5.2.2 Updated spike vendor and not a Parent Spike
- Added DoD QSM Version 3.0 Requirement Tables
- Added S-Q-004 Manual Integration Policy and example documentation
- Removed reference to LabNet to LIMS

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Table 1.

Example: Retention Times (minutes)

Compound	C18 Column	Phenyl Hexyl Column
HMX	4.48	17.50
RDX	6.71	12.28
1,3,5-Trinitrobenzene	9.15	11.54
1,3-Dinitrobenzene	11.07	10.14
Nitrobenzene	12.44	8.84
2,4,6-Trinitrotoluene	15.24	15.68
Tetryl	13.25	15.68
2,4-Dinitrotoluene	17.95	12.64
2-Amino-4,6-Dinitrotoluene	16.50	13.70
2,6-Dinitrotoluene	17.49	12.64
4-Amino-2,6-Dinitrotoluene	15.84	13.38
2-Nitrotoluene	20.96	10.83
4-Nitrotoluene	22.63	10.83
3-Nitrotoluene	24.34	11.12
1,2-Dinitrobenzene (surrogate)	9.55	12.06
Nitroglycerine**	14.60	*
PETN**	29.4	*

*To be determined
**Analyzed at a wavelength of 210 nm

Attachment 1.

Example: Reporting Limits, MDLs, and Statistical Control Limits

Method Limit Report using report code 8330

Test Long Description	TMX	Units	MDL	RL	LCSLL	LCSUL	LCSRPD	Limits SLL	Limits SUL
Method: Explosives by 8330 (HPLC) (8330)									
1,2-Dinitrobenzene (surr)		ug/L						66	144
1,3-Dinitrobenzene		ug/L	0.033	0.16	79	115	20		
1,3,5-Trinitrobenzene		ug/L	0.039	0.16	77	130	20		
2-Amino-4,6-Dinitrotoluene		ug/L	0.035	0.31	87	117	20		
2-Nitrotoluene		ug/L	0.082	0.31	77	113	20		
2,4,6-TNT		ug/L	0.036	0.16	75	145	20		
2,4-Dinitrotoluene		ug/L	0.032	0.31	81	116	20		
2,6-Dinitrotoluene		ug/L	0.071	0.31	85	115	20		
3-Nitrotoluene		ug/L	0.137	0.31	80	112	20		
4-Amino-2,6-Dinitrotoluene		ug/L	0.074	0.31	87	117	20		
4-Nitrotoluene		ug/L	0.082	0.31	76	113	20		
HMX		ug/L	0.122	0.31	82	116	20		
MNX		ug/L	0.064	0.16	74	117	20		
Nitrobenzene		ug/L	0.032	0.16	81	106	20		
RDX		ug/L	0.077	0.16	86	124	20		
Tetryl		ug/L	0.065	0.39	84	118	20		
1,2-Dinitrobenzene (surr)		ug/L						66	144
1,3-Dinitrobenzene		ug/L	0.033	0.16	79	115	20		
1,3,5-Trinitrobenzene		ug/L	0.039	0.16	77	130	20		
2-Amino-4,6-Dinitrotoluene		ug/L	0.035	0.31	87	117	20		
2-Nitrotoluene		ug/L	0.082	0.31	77	113	20		
2,4,6-TNT		ug/L	0.036	0.16	75	145	20		
2,4-Dinitrotoluene		ug/L	0.032	0.31	81	116	20		
2,6-Dinitrotoluene		ug/L	0.071	0.31	85	115	20		
3-Nitrotoluene		ug/L	0.137	0.31	80	112	20		
4-Amino-2,6-Dinitrotoluene		ug/L	0.074	0.31	87	117	20		
4-Nitrotoluene		ug/L	0.082	0.31	76	113	20		
HMX		ug/L	0.122	0.31	82	116	20		
MNX		ug/L	0.064	0.16	74	117	20		
Nitrobenzene		ug/L	0.032	0.16	81	106	20		
RDX		ug/L	0.077	0.16	86	124	20		
Tetryl		ug/L	0.065	0.39	84	118	20		
1,2-Dinitrobenzene (surr)	TCLP Le	ug/L						62	159
1,3-Dinitrobenzene	TCLP Le	ug/L	0.16	0.16	79	115	20		
1,3,5-Trinitrobenzene	TCLP Le	ug/L	0.16	0.16	77	130	20		
2-Amino-4,6-Dinitrotoluene	TCLP Le	ug/L	0.31	0.31	87	117	20		
2-Nitrotoluene	TCLP Le	ug/L	0.31	0.31	77	113	20		
2,4,6-TNT	TCLP Le	ug/L	0.16	0.16	75	145	20		
2,4-Dinitrotoluene	TCLP Le	ug/L	0.31	0.31	77	123	20		
2,6-Dinitrotoluene	TCLP Le	ug/L	0.31	0.31	85	115	20		
3-Nitrotoluene	TCLP Le	ug/L	0.31	0.31	80	112	20		
4-Amino-2,6-Dinitrotoluene	TCLP Le	ug/L	0.31	0.31	87	117	20		

Method Limit Report using report code 8330

Test Long Description	TMX	Units	MDL	RL	Limits LCSLL	LCSUL	LCSRPD	SLL	SUL
Method: Explosives by 8330 (HPLC) (8330)									
4-Nitrotoluene	TCLP Le	ug/L	0.31	0.31	76	113	20		
HMX	TCLP Le	ug/L	0.31	0.31	82	116	20		
MNX	TCLP Le	ug/L	0.16	0.16	74	117	20		
Nitrobenzene	TCLP Le	ug/L	0.16	0.16	81	106	20		
RDX	TCLP Le	ug/L	0.16	0.16	86	124	20		
Tetryl	TCLP Le	ug/L	0.39	0.39	84	118	20		
1,2-Dinitrobenzene (surr)	SPLP Le	ug/L						62	159
1,3-Dinitrobenzene	SPLP Le	ug/L	0.16	0.16	79	115	20		
1,3,5-Trinitrobenzene	SPLP Le	ug/L	0.16	0.16	77	130	20		
2-Amino-4,6-Dinitrotoluene	SPLP Le	ug/L	0.31	0.31	87	117	20		
2-Nitrotoluene	SPLP Le	ug/L	0.31	0.31	77	113	20		
2,4,6-TNT	SPLP Le	ug/L	0.16	0.16	75	145	20		
2,4-Dinitrotoluene	SPLP Le	ug/L	0.31	0.31	77	123	20		
2,6-Dinitrotoluene	SPLP Le	ug/L	0.31	0.31	85	115	20		
3-Nitrotoluene	SPLP Le	ug/L	0.31	0.31	80	112	20		
4-Amino-2,6-Dinitrotoluene	SPLP Le	ug/L	0.31	0.31	87	117	20		
4-Nitrotoluene	SPLP Le	ug/L	0.31	0.31	76	113	20		
HMX	SPLP Le	ug/L	0.31	0.31	82	116	20		
MNX	SPLP Le	ug/L	0.16	0.16	74	117	20		
Nitrobenzene	SPLP Le	ug/L	0.16	0.16	81	106	20		
RDX	SPLP Le	ug/L	0.16	0.16	86	124	20		
Tetryl	SPLP Le	ug/L	0.39	0.39	84	118	20		
1,2-Dinitrobenzene (surr)	Solid	ug/Kg						80	121
1,3-Dinitrobenzene	Solid	ug/Kg	5.0	100.	86	112	30		
1,3,5-Trinitrobenzene	Solid	ug/Kg	14.4	100.	82	125	30		
2-Amino-4,6-Dinitrotoluene	Solid	ug/Kg	12.1	200.	90	112	30		
2-Nitrotoluene	Solid	ug/Kg	31.8	200.	88	114	30		
2,4,6-TNT	Solid	ug/Kg	15.2	100.	67	152	30		
2,4-Dinitrotoluene	Solid	ug/Kg	14.4	100.	87	114	30		
2,6-Dinitrotoluene	Solid	ug/Kg	25.4	200.	90	112	30		
3-Nitrotoluene	Solid	ug/Kg	32.5	200.	89	115	30		
4-Amino-2,6-Dinitrotoluene	Solid	ug/Kg	85.6	200.	88	119	30		
4-Nitrotoluene	Solid	ug/Kg	30.2	200.	86	114	30		
HMX	Solid	ug/Kg	30.2	200.	86	117	30		
MNX	Solid	ug/Kg	23.0	100.	70	130	30		
Nitrobenzene	Solid	ug/Kg	16.9	100.	90	109	30		
RDX	Solid	ug/Kg	33.3	200.	90	115	30		
Tetryl	Solid	ug/Kg	117.	250.	60	130	30		
1,2-Dinitrobenzene (surr)	Wipe	ug/Wipe						80	121
1,3-Dinitrobenzene	Wipe	ug/Wipe	1.0	1.0	86	112	30		
1,3,5-Trinitrobenzene	Wipe	ug/Wipe	1.0	1.0	82	125	30		
2-Amino-4,6-Dinitrotoluene	Wipe	ug/Wipe	2.0	2.0	90	112	30		

Method Limit Report using report code 8330

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
Method: Explosives by 8330 (HPLC) (8330)									
2-Nitrotoluene	Wipe	ug/Wipe	2.0	2.0	88	114	30		
2,4,6-TNT	Wipe	ug/Wipe	1.0	1.0	67	152	30		
2,4-Dinitrotoluene	Wipe	ug/Wipe	1.0	1.0	87	114	30		
2,6-Dinitrotoluene	Wipe	ug/Wipe	2.0	2.0	90	112	30		
3-Nitrotoluene	Wipe	ug/Wipe	2.0	2.0	89	115	30		
4-Amino-2,6-Dinitrotoluene	Wipe	ug/Wipe	2.0	2.0	88	119	30		
4-Nitrotoluene	Wipe	ug/Wipe	2.0	2.0	86	114	30		
HMX	Wipe	ug/Wipe	2.0	2.0	86	117	30		
MNX	Wipe	ug/Wipe	1.0	1.0	70	130	30		
Nitrobenzene	Wipe	ug/Wipe	1.0	1.0	90	109	30		
RDX	Wipe	ug/Wipe	2.0	2.0	90	115	30		
Tetryl	Wipe	ug/Wipe	2.5	2.5	60	130	30		

Attachment 2.

Example: Standards, Working Spike, and Working Surrogate Concentrations

STL CHICAGO
NITROAROMATICS AND NITROAMINES BY HPLC
CALIBRATION STANDARDS (ug/mL)

COMPOUND	LEVEL 1	LEVEL2	LEVEL 3	LEVEL 4	LEVEL 5	LEVEL 6
HMX	0.020	0.050	0.100	0.200	0.400	1.00
RDX	0.020	0.050	0.100	0.200	0.400	1.00
1,3,5-TNB	0.020	0.050	0.100	0.200	0.400	1.00
1,2-DNB	0.020	0.050	0.100	0.200	0.400	1.00
1,3-DNB	0.020	0.050	0.100	0.200	0.400	1.00
TETRYL	0.040	0.100	0.200	0.400	0.800	2.00
NITROBENZENE	0.020	0.050	0.100	0.200	0.400	1.00
2,4,6-TNT	0.020	0.050	0.100	0.200	0.400	1.00
2-AM-4,6-DNT	0.040	0.100	0.200	0.400	0.800	2.00
4-AM-2,6-DNT	0.040	0.100	0.200	0.400	0.800	2.00
2,4-DNT	0.020	0.050	0.100	0.200	0.400	1.00
2,6-DNT	0.040	0.100	0.200	0.400	0.800	2.00
2-Nitrotoluene	0.040	0.100	0.200	0.400	0.800	2.00
3-Nitrotoluene	0.040	0.100	0.200	0.400	0.800	2.00
4-Nitrotoluene	0.040	0.100	0.200	0.400	0.800	2.00
MNX	0.020	0.050	0.099	0.198	0.396	0.99
PETN*	0.040	0.100	0.200	0.400	0.800	2.00
Nitroglycerine*	0.040	0.100	0.200	0.400	0.800	2.00

*Compounds are not part of routine 8330 list and would require a separate analytical run to report

SPIKE CONCENTRATIONS:

HMX	2.0 ug/mL
RDX	2.0
1,3,5-TNB	2.0
1,3-DNB	2.0
TETRYL	4.0
NITROBENZENE	2.0
2,4,6-TNT	2.0
2-AM-4,6-DNT	2.0
4-AM-2,6-DNT	4.0
2,4-DNT	2.0
2,6-DNT	4.0
2-NITROTOLUENE	4.0
3-NITROTOLUENE	4.0
4-NITROTOLUENE	4.0
MNX	5.0
Petn	1.0
Nitroglycerin	1.0

SURROGATE:

	2.0 ug/mL
1,2-DNB	

Attachment 3.

STL Corporate Procedure, P-T-001, 'Selection of Calibration Points'

Approvals and Signatures

Senior Vice President & Chief Operating Officer:	Dr. Keith C. Wheatstone	Date: 10/6/2004
Vice President, Client and Operations Services:	Dr. Charles W. Carter	Date: 10/6/2004
Technology Director:	Dr. Richard Burrows	Date: 9/8/2004

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1.0 PURPOSE

This policy describes Severn Trent Laboratories (STL) requirements for determination of the number of points, and removal of points from calibration curves.

2.0 SCOPE

Applies to all multi-level initial calibrations.

3.0 POLICY

3.1 If the number of data points required for an initial calibration is defined in the method, Quality Assurance (QA) plan, published report, or previously approved Standard Operating Procedure (SOP) that is what will be used.

3.2 In the cases not defined in Section 1, the number of data points will be determined by the technical director based on the Data Quality Objectives (DQOs) for precision and accuracy to be met by the method.

Examples:

A. Need to analyze a new pesticide in water and a published method does not exist. The data will be used to screen samples by UV-HPLC at a waste site for further remediation, using DQOs that require precision/accuracy of ± 50%.

The Technical director selects 2 data points to represent the range of the expected concentration of pesticide and based on 4 Laboratory Control Samples (LCS), the recoveries ranged from 78-104%. Therefore, 2 data points are sufficient for initial calibration for this method.

NOTE: Calibration curves with less than 3 points should only be used after discussion with the client that the data quality objectives will be met.

B. Same compound as above but being measured in laboratory for meeting regulatory limit of 0.05 mg/L in water. Precision and accuracy of ± 20% required.

A five-point calibration is used, based on similar requirements in published methods with similar objectives and the high level of precision and accuracy required.

As noted above for methods where technical director selects the number of data points to meet DQOs for precision and accuracy, the 4 LCS used in the demonstration of capability will be used to assure those DQOs are met. The SOP will then be approved by the Quality Assurance (QA) Manager.

3.3 Removal of Points from a Calibration Curve

3.3.1 Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted unless an injection or instrument problem confined to that point can be clearly documented as described below. Removal of points for individual analytes from levels other than the highest and lowest is not permitted in any event.

3.3.2 If the analyst can document that a level is not valid because of an injection or instrument problem confined to that run, the level may be excluded if the curve still has sufficient levels, or the run may be repeated once only. The whole level (all compounds) must be

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removed or replaced. The curve is evaluated with the level removed or replaced. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve reanalyzed. Corrective action may include, but is not limited to, instrument maintenance and/or re-preparation of standards.

3.3.3 One of the following conditions must be satisfied to allow removal or replacement of a level:

- The data file is corrupted and unusable or the run is interrupted before completion.
- The analyst observes and documents a problem such as leaking of a purge vessel.
- For internal standard methods, the recovery of the internal standards is less than 70% or greater than 130% of the recovery in the other standards, or the amount of analyte recovered is less than 70% or greater than 130% of the expected values (indicating an improperly made up standard).
- For external standard methods, the unit response of the analyte is less than 70% or greater than 130% of the average unit response for the analyte in the other calibration standards (indicating an improperly prepared standard or bad injection).

3.3.4 When using autosamplers with discrete sample pathways for different samples (such as 16 port purge and trap autosamplers) the level to be replaced must be reanalyzed on the same port or that port must be excluded from sample analysis until corrective action is performed and verified by successful analysis of a continuing calibration standard on that port.

3.3.5 The reason for replacing the level **must** be documented in the run log. The fact that the curve passes criteria with the level removed is **not** alone sufficient evidence to document an injection or instrument problem confined to the level.

3.3.6 Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed then the reporting limit is raised to be equivalent to the lowest level used in the calibration curve. In any event the number of levels remaining in the calibration must be at least that required by the method.

3.3.7 Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method.

4.0 RESPONSIBILITIES

All STL associates utilizing methods involving multi-point calibrations are required to follow this policy.

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5.0 ATTACHMENTS

Not Applicable.

6.0 REVISION HISTORY

Revision 3: Updated by Richard Burrows, Technology Director; 9/8/2004.
Section 3.2: Amended 'NOTE'.
Section 3.3.3, bullet #4, text reworded for clarification.

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Attachment 4.

Example: Analysis Run Log / Maintenance Log

Extraction Date:_____ **STL Chicago** Page No.:_____

Solvent:_____ **Explosives Extraction Record** Analyst Initials:_____

LabNet Batch No.:_____

Matrix: a. Water b. Soil Extraction Method: SW-846 8330 / 8332
c. Other:_____

	STL #	Sample ID	ICOC	Initial Volume (mLs) / Weight (g)	Final Volume (mLs)	Multipliers		
						Surr.	Spike	Split
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								
11								
12								
13								
14								
15								
16								
17								
18								
19								
20								
21								
22								
23								
24								

Note: Soil samples are dried prior to the taking of a sample aliquot for extracting.

Comments:_____

Surrogate:_____ Volume:_____ Std. ID#:_____

LCS/MS Solution:_____ Volume:_____ Std. ID#:_____

LCS/MS Solution:_____ Volume:_____ Std. ID#:_____

Analyst Signature:_____ Date:_____

Reviewer Signature:_____ Date:_____

Analysis Custody Record

Sample(s)	Date/Time Out	Date/Time In	Analyst	Sample(s)	Date/Time Out	Date/Time In	Analyst

Instrument #43

STL Chicago
HPLC Analysis Log

Page #: 1

Analyst:_____ Method:_____ Column:_____

Queue:_____ Inj. Vol.:_____ Flow:_____ Column Temp.:_____

Mobile Phase:_____ Pressure:_____ Wavelength:_____

Rep. #	Sample Description	Dil. Factor	Injection Date/Time	Comments

Reviewer:_____ Date:_____

STL Chicago
HPLC Instrument Maintenance Log

Page No.:_____
Instrument No.:_____

Routine/Informal Maintenance includes: Periodically check all pump seals for leaks.

Entry No.:_____

Date of Maintenance:_____ Analyst:_____

___ Changed Purge Valve Frit
___ Changed Pre-Column Filter
___ Flushed Column with _____
___ Changed Lamp
___ Changed Column
___ Repair / Replaced Pump Seal(s)
___ Other (explain)

Explain/Actions Taken:_____

Demonstration of Control:
___ CCV analyzed and in-control.
___ Samples Reanalyzed.
___ Other (explain)

Explain:_____

Entry No.:_____

Date of Maintenance:_____ Analyst:_____

___ Changed Purge Valve Frit
___ Changed Pre-Column Filter
___ Flushed Column with _____
___ Changed Lamp
___ Changed Column
___ Repair / Replaced Pump Seal(s)
___ Other (explain)

Explain/Actions Taken:_____

Demonstration of Control:
___ CCV analyzed and in-control.
___ Samples Reanalyzed.
___ Other (explain)

Explain:_____

Reviewer Signature:_____ Date:_____

Attachment 5.

Example: Data Review Checklist

STL Chicago

EGC / HPLC / GC VOA DATA REVIEW CHECKLIST

Site Name:_____ Primary Reviewer:_____ Review Date:_____
JOB Number:_____ Secondary Reviewer:_____ Review Date:_____
No. of Samples/Matrix: a) ____ WATER b) _____ SOIL c) _____ TCLP / SPLP d) _____ Other (_____)
Review Level: a) Full b) Cursory Method: a) GC VOA _____ b) GC _____ c) HPLC _____ d) Other (_____)
Extr. Method: a) SW 3510 b) SW 3520 c) SW 3550 d) SW 3580 e) SW 3541 f) SW 5030 /5035 g) CLP____ h) Other (_____)

CAR's _____ Std. Traceability _____ TASK		PRI REV	SEC REV	COMMENTS
LAB CHRON:	1) Matches Raw Data (Form 4, 8)			
	2) Samples which were Re-Analyzed or Re-Extracted were Re-Logged into LabNet			
	3) Sample Hold Times were Met			
	4) Proper Prep Links were created			
PROJ. REQ.MET:	1) List of Compounds			
	2) Sample Detection Limits Met			
	3) Method Blank Detection Limits Met			
LabNet Batch Status Report Displays Data at RVWD Status Incomplete JOB Status Report reveals no Outstanding Data				
FORM 1:	1) Matches Quant Report			
	2) Matches LabNet Report			
FORM 2: Surrogate Recoveries Within Limits Statistical Limits _____ Method Limits _____ Project Limits _____(S-F10 used to Clone By Project)				
FORM 3: MS/MSD Recoveries Acceptable Statistical Limits _____ Method Limits _____ Project Limits _____(S-F10 used to Clone By Project)				
FORM 3: BS Recoveries Acceptable Statistical Limits _____ Method Limits _____ Project Limits _____(S-F10 used to Clone By Project)				
Initial Calibration Criteria Met				
Daily Calibration (CCV) Criteria Met				
Form 10:	1) Retention Window (RT) Criteria Met			
	2) Concentrations Correct			
Correct Usage of FLAGS				
RAW DATA:	1) Raw Data Verified/Complete			
	2) Raw Data Matches Forms			
NARRATIVE:	1) Holding Times			
	2) Method References			
	3) % Recoveries / RPD's			
	4) Analytical Difficulties/Typos			

COMMENTS ON REVERSE

COMMENTS:

REVIEW CYCLE	REASON
1	
2	
3	
4	

STL Chicago
GC/HPLC Data Review Checklist

Project: _____ **Job #:**_____ **Method:**_____

Reviewer (1):_____ **Date:**_____

Reviewer (2):_____ **Date:**_____

Sublist:_____
Instruments (Primary/Confirmation):_____
Cleanups:_____
CAR (Y/N):_____

Target Review

Reviewer 1	Reviewer 2	
____	____	Chromatography is acceptable.
____	____	Chromatograms are scaled properly.
____	____	All peaks are labeled properly.
____	____	All initial calibrations are within control limits ($\leq$ 20% RSD; Correlation Coefficient $\leq$ 0.995).
____	____	Second Source Verification is in control (85% - 115%).
____	____	All continuing calibrations are within control limits ($\pm$ 15% difference).
____	____	All retention times are within their windows.
____	____	All method blanks are clean.
____	____	Calculations verified.
____	____	Verify samples are quantified using the proper ICAL.
____	____	Before and after chromatograms produced for all manual integrations.

Comments:_____

Updating Results in LabNet

____	____	Reagent codes are correct.
____	____	Batch test results match quant reports.
____	____	Batch cloned for project limits.
____	____	Proper prep links were created (including TCLP link).
____	____	Each required target compound diplays "0" when data is reported.
____	____	Client information has been checked for correct list, reporting limits, special requirements.
____	____	Job notes (CTRL F12) for the job have been reviewed.

Comments:_____

GC/HPLC Data Review Checklist

QC Data

____ ____ All LCS/LCD recoveries (and RPDs) are within the required control limits (verify calc.).
____ ____ All surrogate recoveries are within the required control limits (verify calc).
____ ____ All MS/MSD recoveries and RPDs are within the required control limits (verify calc.).

Comments:_____

Note: Anything out of the ordinary must be commented on and be approved by the Unit Leader/Section Manager for inclusion in the Case Narrative.

____ RG LabChron/Report Review Initial/Date _____

Comments:

STL Chicago
GC/HPLC Data Review Checklist - "CLP-like"
(SW-846 and 40 CFR)

Client: _____ **JOB#:** _____ **Test:**

Reviewer(1): _____ **Date:**

Reviewer(2): _____ **Date:**

COC/Deliverable

Reviewer 1	Reviewer 2	
____	____	Chain-of-custody has been checked to ensure that the proper analyte list is reported.
____	____	All special project requirements are met, i.e., control limits, forms, etc...

Comments: _____

Updating Results in Labnet

____	____	Reagent codes are correct.
____	____	Batch test results match quant. reports.
____	____	Batch cloned for project limits.
____	____	Proper prep links were created (including TCLP link).
____	____	Each required target compound displays "0" when data is reported.
____	____	Client information has been checked for correct list, reporting limits, special requirements.
____	____	Job Notes (CTRL F12) for the job have been reviewed.

Form 1/Associated Data

____	____	Observe chromatograms, check for obvious chromatography errors.
____	____	Check form information for correctness (JOB #, reporting limit, dilution factor, matrix, flags, etc....)
____	____	Check values reported. In an "E" is present, there must be another dilution; if a value is reported, review the chromatogram; if a "J" is reported, review the chromatogram; if an "I" is reported, there must be another dilution run.
____	____	Check that all JOB #'s on the chromatograms match quant report and data on quant report is correct.
		Check that confirmation chromatograms agree with quantitation chromatograms.
____	____	All method blanks are clean.
____	____	All OPC file information is present and correct (matrix, final volume, %sol present for soils).
____	____	Before and after chromatograms are present for all Manual integrations and are dated/initialed by analyst.

Comments: _____

Form 2/Associated Data

____	____	Requested surrogates were used.
____	____	All surrogate recoveries are within control limits. If not, proper corrective actions have been taken and are documented. [Samples with surrogates outside of control limits may not require re-analysis but must be evaluated, flagged, and discussed in the case narrative. If not specified by the client, both (if applicable) surrogate recoveries must be within statistical control limits. Surrogates associated with the method blank and blank spikes should be within control.]
____	____	Confirm all samples and QC for that batch are represented.
____	____	Confirm correct matrix.
____	____	Correct surrogate concentration used for calculating % Recovery. Verify calculations.

Comments: _____

Form 3/Associated Data

Reviewer 1	Reviewer 2	
____	____	Blank spike and blank spike duplicate have the proper batch number, and the proper matrix
____	____	All blank spike/blank spike duplicate recoveries and RPDs are within control limits. If not, proper corrective actions have been taken and documented. Flag outliers for the Case Narrative and provide documentation.
____	____	Confirm that the matrix spike and matrix spike duplicate data correlates with the unspiked analysis.
____	____	All matrix spike/matrix spike duplicate recoveries and RPDs are within control limits. If not, proper corrective actions have been taken and documented. Flag outliers for the Case Narrative.
____	____	Confirm correct matrix and sample ID.
____	____	Correct spike concentration used for calculating % Recovery. Verify calculations.

Comments:_____

_____

Form 4/Associated Data

____	____	Check all header information, extraction date, analysis date and time, instrument and column IDs.
____	____	Confirm all samples associated with the blank are present.
____	____	Confirm all blank summaries are present for all samples/matrices in the data package.
____	____	Confirm proper matrix and extraction method.
____	____	Sulfur cleanup performed (not applicable to some methods)

Comments:_____

_____

Endrin/DDT Breakdown

____	____	All breakdown criteria is met (<15% for DDT and/or Endrin) for 608 and 8081A only.

Comments:_____

_____

Initial Calibration/Associated Data (Form 6)

____	____	Method SW-846: All % RSDs are <20% (5-pt. minimum)
____	____	Method 40CFR: All %RSDs are <10% (3-pt. minimum).
____	____	Recalculate a few %RSDs.
____	____	All header information is correct (times, dates).
____	____	Second Source Verification (SSV) is in control (85%-115%)

Comments:_____

_____

Continuing Calibration Verification/Associated Data (Form 7) - Standards that are outside the control limits must be approved by the Section Manager prior to the reporting of any data.

____	____	All header information is correct. Dates and times of initial standards and continuing standards are correct.
____	____	All retention times are within their windows, those that are outside are marked for Case Narrative.
____	____	Ave. CFs match from ICAL (Form 6) Ave CFs.
____	____	All %Ds are within control limits. If not, proper corrective actions have been taken and documented.
____	____	All Form 7's associated with the samples and QC are present.

Comments:_____

_____

Form 10/Associated Data

Reviewer 1	Reviewer 2	
____	____	Confirm that all analytes which are reported as being detected on the Form 1 are present.
____	____	Confirm that all retention times of analytes reported as positive hits are within their retention time window, and if they aren't, why the analyst reported them must be documented in the comment section.
____	____	The GC columns are marked Y/N for quantitation/confirmation (applicable to 8330 only).

Comments:_____

Additional Data

____	____	All necessary runlogs are present and contain the proper sequences.
____	____	All necessary extraction records are present.
____	____	All required holding times were met for samples dilutions and QC.
____	____	Chronology of data is correct.
____	____	Dates and times of analysis are correct.
____	____	Verify samples are quantitated using the proper ICAL.

Comments:_____

____ RG LabChron/Report Review Initial/Date _____

Attachment 6.

Solid Phase Extraction (SPE) Method 3535

EPA Method 3535
Explosives from aqueous samples

I. Materials

Strata SPE: SDBL 500 mg/ 6mL
Part Number: 8B-S014-HCH
Conditioning Solvent: Methylene Chloride (DCM), Acetonitrile, DI Water
Wash Solvent: DI Water
Extraction Solvent: Acetonitrile

II. Solid Phase Extraction Method

A. Condition: Slowly pass through the cartridge (3-6ml /min)

1. Rinse with DCM (about 18mL) with no vacuum.
2. 1 column volume of Acetonitrile (about 6mL)
3. 1 column volume of DI water (about 6mL)

B. Load Sample:

For processing large volume samples greater than 6mL; refer to Phenomenex Strata publication entitled "*Processing Large Volume Samples with Strata SPE Cartridges*" located on next page.

C. Wash:

Wash the sample with three column volumes (about 18mL) of DI Water. Dry thoroughly for 30-60 seconds to insure removal of aqueous wash.

D. Elute: (about 2 minutes)

1. Rinse the sample bottle with 5mL of Acetonitrile:MeOH 80:20 and decant into the syringe barrel reservoir.
2. Engage vacuum until the Acetonitrile just begins to drip through the sorbent, then stop and allow remaining volume of Acetonitrile to drain through by gravity into the collection tube. Apply vacuum to get the final drops.

See Section 7.3.1.10 for preparation of sample for analysis.

Processing Large Volume Samples with Strata SPE Cartridges

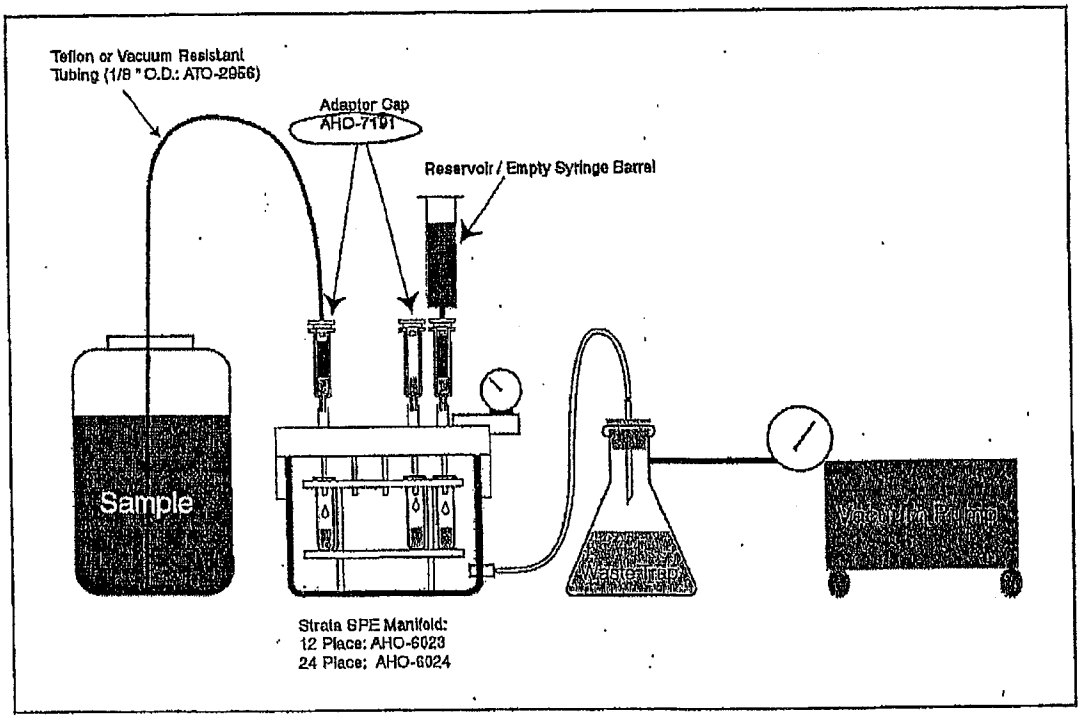
A major benefit of SPE is its ability to concentrate trace amounts of analyte from very dilute, large volume samples. Unfortunately these samples are often several times larger than the reservoir capacity of the SPE cartridge. Several strategies have proven most useful in dealing with these large volume samples.

1. Apply the sample to the cartridge in multiple aliquots.

2. Attach a separate, large-volume reservoir to the top of the SPE cartridge using an adapter cap.

3. Connect the SPE cartridge directly to the sample reservoir using a piece of tubing. The applied vacuum creates a suction that draws the sample from the sample reservoir through the tubing, into the SPE cartridge and through the sorbent bed. Vacuum tight connection between the tubing and the SPE cartridge adapter is critical.

Reminder: A cartridges' retention capacity is strictly related to the mass of sorbent packed into the cartridge and is unaffected by the so-called "reservoir" volume capacity of the cartridge. For example, a 500 mg / 3 ml tube has the exact same retention capacity as a 500 mg / 6 ml, or a 500 mg / 12 ml.



Attachment 7.

DoD QSM Version 3.0 Requirements Tables

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Organics (GC/HPLC)

QC Check	Definition	Purpose	Evaluation
Breakdown Check 8081A: Endrin, DDT 8270C: DDT	Analysis of s standard solution containing Endrin and DDT. Area counts of these compounds and their breakdown products are evaluated to assess instrument conditions.	To verify the inertness of the injection port because DDT and Endrin are easily degraded in the injection port.	If degredation of either DDT o Endrin exceeds method–specifi criteria, corrective action must be taken before proceeding with calibration
Confirmation of positive results (organics only)	Use of alternative analytical techniques (another method, dissimilar column, or different detector such as MS detector) to validate the presence of target analytes identified	To verify the identification of an analyte	This is a required QC procedure. All positive results must be confirmed.
CCV	This verification of the initial calibration that is required during the course of analysis at periodic intervals. Continuing calibration applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models	To verify that instrument response is reliable, and has not changed significantly from the current ICAL	If the values for the analytes are outside the acceptance criteria, the initial calibration may not be stable. Results associated with out-of-control CCV results require reanalysis or flagging
Demonstrate Acceptable Analyst Capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision	To establish the analysts' ability to produce data of acceptable accuracy and precision	The average recovery and standard deviation of the replicate must be within designated acceptance criteria.
Duplicate Sample	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are taken and prepared and analyzed identically.	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intralaboratory analytical process for a specific sample matrix	To provide information on the heterogeneity of the sample matrix. The greater the heterogeneity of the matrix, the greater the RPD between the sample and the duplicate
ICAL	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method	To establish a calibration curve for the quantification of the analytes of interest	Statistical procedures are used to determine the relationship between the signal response and the known concentration of analytes of int The ICAL must be successful b any samples or other QC check samples can be analyzed.
Internal Standards	A known amount of standard added to all standards and samples as a reference for evaluating and controlling the precision and bias of the applied analytical method	To verify that the analytical system is in control	Any sample associated with out-of-control results must be reanalyzed.
LCS containing all analytes required to be reported	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern.	To evaluate method performance by assessing the ability of the lab/analyst to successfully recover the target analytes from a control (clean) matrix.	This is a required QC Check. The inability to achieve acceptable recoveries in the LCS indicate problems with the accuracy/bias of the measurement system.
MS	A sample prepared by adding a know amount of targeted analyte(s) to an aliquot of a specific environmental sample	To assess the performance of the method as applied to a particular matrix	The lack of acceptable recoveries in the matrix spike often points to problems with the sample matrix. One test of this is a comparison to the LCS recoveries. If the corresponding LCS recoveries are within acceptable limits, a matrix effect is likely. The lab should not correct for recovery; only report the results of the analyses and the associated MS results and indicate that the results from these analyses have increased uncertainty
MSD	A 2nd replicate MS prepared in the lab, spiked with an identical, known amount of targeted analyte(s), and analyzed to obtain a measure of the precision of the recovery for each analyte	To assess the performance of the method as applied to a particular matrix and provide information of the homogeneity of the matrix.	When compared to the MS, the MSD will provide information on the heterogeneity of the sample matrix.

Table B-1 Cont.			
QC Check	**Definition**	**Purpose**	**Evaluation**
MDL Verification Check	A low-level spike taken through the prep and analytical steps at approximately 2x the MDL used to verify that the laboratory can detect analytes at the calculated MDL	To validate the MDL on an ongoing basis	If the MDL verification check fails, reprep/reanalyze at a higher level to set a higher MDL or the MDL study must be repeated.
MB	A sample of a matrix similar to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results.	To assess background interferences or contamination in the analytical system that might lead to high bias or false positive data.	This QC is used to measure lab accuracy/bias. The MB could indicate whether contamination is occurring during sample prep and analysis. If analytes are detected > ½ RL, reanalyze or B-Flag results for all samples in prep batch. For common lab contaminants, no analytes detected > RL. See DoD Box D-5; & Sec. D.1.1.1
MDL Study	The process to determine the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.	MDLs must be established prior to sample analysis. The RL or LOQ is at least 3x the MDL. Used in combination with the MDL verification check to validate the MDL on an ongoing basis.
RT window position establishment for each analyte (chromatographic methods only)	Determination of the placement of the RT window (start/stop time) of each analyte or group of analytes as it elutes through the chromatographic column so that analyte identification can be made during sample analysis. This is done during the initial calibration	To idendify analytes of interest	Incorrect window position may result in false negatives, require additional manual integrations, and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified.
RT window verification for each analyte (chromatographic methods only)	A standard is used to verify that the width and position of the RT windows are valid so that accurate analyte identification can be made during sample analysis	To minimize the occurance of both false positive and false negative results at each calibration verification.	The peaks from the standard used are compared to the RT window established during the ICAL to verify that the analytes of interest still fall within the window.
RT window width calculate for each analyte and surrogate (non-MS chromatographic methods only)	Determine the length of time between the sample injection and the appearance of a peak at the detector. The total length of time (window) is established for each analyte or groups of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.	To ensure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the standards and sample matrix to be analyzed. It is done to minimize the occurrence of both false positive and false negative results	Used to evaluate continued system performance. Tight RT windows may result in false negatives and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide RT windows may result in false positive results that cannot be confirmed upon further analysis.
Second source calibration verification	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration	The concentration of the 2nd source calibration verification, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. This independent verification of the ICAL must be acceptable before sample analysis can begin.
Surrogate spike (organic analysis only)	A pure substance with properties that mimic the analyte of interest. Surrogates are compounds unlikely to be found in environmental samples to evaluate analytical efficiency by measuring their % Recovery.	To assess the ability of the method to successfully recover specific non-target analytes from an actual matrix.	Whereas the MS is normally done on a batch-specific basis, the surrogate spike is done on a sample-specific basis. Taken with the information derived from other spikes (LCS; MS), the bias in the analytical system can be determined.

Notes:

1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-2: Organic Analysis by GC and HPLC - Methods 8015; 8081; 8082; 8141; 8151; 8310; 8330

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
IDOC	Per Instrument/Analyst	DoD acceptance criteria if available; otherwise method specific criteria	Correct / Repeat for those analytes which failed criteria	NA
MDL	Annually or quarterly MDL Checks performed	40 CFR 136B; MDL verification checks must produce a signal at least 3x the instrument's noise level.	Run MDL check at higher level and set MDL higher or reconduct MDL study	NA
RT window	At method set-up and after major instrument maintenance	RT width is ± 3x standard deviation for each analyte RT from 72-hour study	NA	NA
Breakdown check (Endrin/DDT-8081 only)	Daily prior to analysis of samples	Degradation ≤ 15% for both Endrin & DDT	Correct problem then repeat breakdown check	NA
ICAL	Initial 5-point calibration prior to sample analysis	One of the options below (Except for 8082. which may only use Option 1 or 2) **Option 1:** RSD for each analyte ≤ 20% **Option 2:** linear least squares regression: r ≥ 0.995 **Option 3:** non-linear regression: Coefficient of determination (COD) $r^2 \geq 0.99$ (6 points shall be used for 2nd order, 7 points shall be used for 3rd order)	Correct problem then repeat initial calibration	NA
2nd Source calibration verification	Once after each initial calibration	Value of 2nd source for all analytes within ± 20% of expected value	Correct problem and verify 2nd source standard. Rerun, if that fails, correct problem and repeat initial calibration.	NA
RT window position establishement for each analyte	Once per ICAL and at the beginning of the analytical shift	Position shall be set using midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift	NA	NA
RT window verification for each analyte & surrogate	Each calibration verification standard	Analyte within established window	Correct problem, then reanalyze all samples analyzed since the last acceptable RT check. If they fail, repeat ICAl and reset RT window	ICAL – NA CCV – apply Q-flag results for analytes ou.. of RT window
Calibration verification (ICV) and continuing (CCV)	ICV – Daily, before sample analysis CCV – After every 10 field samples and at end of analysis sequence. (DoD Box 58: CCV standards shall be at or below the middle of the calibration range)	All analytes within +/- 20% of expected value from ICAL (Data associated with an unacceptable CCV may be fully usable under the following conditions: 1. CCV (high bias) and samples ND, then raw data may be reported with appropriate flag 2. 2. CCV (low bias) and samples exceed maximum regulatory limit/decision level (DoD Box 60: Project specific permission from appropriate DoD personnel is required to report data generated from a run with noncompliant CCV.)	ICV – Correct problem, rerun ICV, if fails, repeat ICAL CCV – Correct problem, repeat CCV and reanalyze all samples since the last good CCV (DoD Box 59...if the lab chooses to demonstrate the success of routine corrective action through the use of 2 consecutive CCVs, then the concentrations of the two CCVs must be a two different levels within the original calibration curve with at least one falling below the middle of the calibration range.)	ICV – NA CCV – apply Q-flag to all results for the specific analyte(s) in all samples since the last acceptable CCV, if reanalysis is not possible
MB	One per prep batch	No analytes detected > ½ RL For common lab contaminants, no analytes ≥ RL	Correct problem, then see criteria in box D-5; if required, reprep/reanalyze MB and all associated samples	Apply B-flag to all results for the contaminated analyte for all samples in the associated prep batch
LCS (containing all analytes to be reported)	One LCS per prep batch	DoD specified QC criteria, if available	Correct problem, reprep/reanalyze the LCS and all samples in the associated prep batch for all failed analytes, if sufficient sample is available	Apply Q-flag to specific analyte(s) in all samples in the prep batch.
MS	One per prep batch per matrix	For matrix evaluation, use DoD specified QC criteria for LCS	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample
MSD or Sample Duplicate	One per prep batch per matrix	RPD ≤ 30% (between MS and MSD or sample and sample duplicate)	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample

Table B-2 cont.				
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**
Surrogate	All field and QC samples	DoD specified QC criteria if available, otherwise method specific criteria or lab's own in-house criteria	For QC and field samples, correct problem, reprep/reanalyze all failed samples in the associated prep batch if sufficient sample material is available. If obvious chromatographic interference with surrogate is present, reanalysis may not be necessary	Apply J-flag for specific analyte(s) in all field samples collected from the same site matrix as the parent. Apply Q-flag to QC samples for specific analyte(s)
Confirmation of Positive Results	All positive results must be confirmed (exceptions: 8081A, toxaphene & technical chlordane 8015B, GRO, DRO	Calibration and QC criteria same for initial or primary column analysis. Results between primary and secondary column RPD $\leq$ 40%	NA Note: Report the higher of the two confirmed results unless overlapping peaks are causing erroneously high results – document in case narrative	Apply J-flag if RPD > 40% or Q-flag if sample is not confirmed. Discuss in the case narrative
Results reported between LOD and LOQ			Apply J-flag to all results between LOD (MDL) and LOQ (RL)	
Manual Integration	When manual integrations are performed	Raw data shall include a complete audit trail for those manipulations, raw data output showing the results of the MI (i.e., chromatograms of manually integrated peaks), and notation of rationale, date, and signature/initials of person performing manual operation.		Apply M-flag to MI data

Notes:
1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

Attachment 8.

STL Corporate Policy, S-Q-4, 'Acceptable Manual Integration Practices' and Example Documentation

Approvals and Signatures

Senior Vice President & Chief Operating Officer:	Dr. Keith C. Wheatstone	Date: 9/20/2004
Vice President, Client and Operations Services:	Dr. Charles W. Carter	Date: 9/20/2004
Corporate Quality Director:	Raymond J. Frederici	Date: 9/20/2004

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1.0 PURPOSE

This document describes STL's policy for proper manual peak integrations and requirements for documentation and review of manual peak integrations performed during the course of analyses.

2.0 SCOPE

This policy shall be enforced and followed throughout the laboratory. It applies to all STL laboratories for any analytical procedure involving identification or quantitation based on peak

analysis (e.g., GC, GC/MS, HPLC, IC). Each laboratory may have supplemental manual integration procedures or an addendum to this policy that describes additional details necessary to implement and enforce this policy. Any supplemental procedure or addendum must adhere to the requirements set forth in this policy.

3.0 POLICY

3.1 Supervisors must ensure proper training to all analysts and data reviewers using peak integration techniques. Analysts and data reviewers using peak integration techniques must be familiar with this policy and the applicable data processing system. This is to ensure that integration parameters are used in a manner that minimizes the need for manual integrations and that circumstances requiring manual integrations are performed in accordance with acceptable practices, documented and reviewed by a peer or supervisor. Audit trails or tracking systems MUST BE activated when the chromatographic system has this feature.

3.2 In some situations, manual integrations are necessary to compensate for imperfect chromatography, but manual integration must be performed ONLY when necessary. Baseline upsets, coelution and peak shape variation can sometimes complicate automatic integration and analyst intervention through manual integration may be required to assure consistency between area assignment for standards and samples.

3.3 Proper consistent manual integration is a critical quality control requirement. Appropriate manual integration is integration that can be technically justified. Manual integrations shall not be used to manipulate analytical results in order to meet method- or project-specific quality control (QC) acceptance criteria. Integration below the baseline is never appropriate. Inappropriate and inconsistent chromatographic peak integration to meet quality requirements is never allowed, nor is it to be used as a substitute for corrective action on the chromatographic system. Willful failure to follow this policy shall result in disciplinary action, up to and including termination.

3.4 The same integration technique must be applied **consistently** to any chromatogram i.e., field samples, calibration standards, calibration verification standards, and other applicable QC, etc., within the same analytical batch affected by the manual integration. Consistency in integration between standards and samples is one of the most important considerations in quantitative chromatographic analysis. Examples of appropriate and improper integration can be found in Appendix I and II.

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4.0 REASONS TO MANUALLY INTEGRATE

4.1 Undetected Peak

Routine mass spectrometer instrument tuning or the analysis of highly contaminated samples sometimes causes the relative abundances of ions of compounds present to deviate from reference criteria causing a peak to go undetected by the data system. A slight shift in chromatographic retention times can result in undetected peaks or false positive identification of compounds. If sample surrogate(s) retention times (RTs) shift, sample peaks need to be reviewed to ensure proper peak identification.

4.2 Incorrect Peak Integration

- Peak has small amount of splitting and the whole peak area was not integrated.
- Peaks close in retention times utilizing the same quantitation ions often integrate together as one peak, for example: ethylbenzene, xylenes; dichlorobenzenes, benzo(b)fluoranthene and benzo(k)fluoranthene.

4.3 Baseline Correction

- Matrix interferences caused by contaminated samples may interfere with calibrated compounds.

4.4 Other Examples of Events Requiring Manual Integration

- Incorrectly identified peak, where the wrong peak is chosen by the data system. This can occur both with the primary and the secondary ions.
- To remove a shoulder from a peak or to integrate a peak that only appears as a shoulder.

5.1 DATA SYSTEM PROCEDURES

5.1 The chromatography system's method integration parameters must be optimized to the greatest extent possible so compounds are properly identified and integrated with minimal operator intervention. (Note: even when integration parameters work properly for calibration standards, the analyst must ensure the integration is appropriate on all samples. The analyst must not assume that the chromatography system will automatically apply the correct integration). When manual integrations are necessary to identify peaks as targets (determine the RT), the calibration standards must be reprocessed after updating the retention times to demonstrate that the data system integration parameters are set properly. The following steps are required:

5.1.1 Process the file using the current data system parameters for the mid-level standard.

5.1.2 Identify all of the target compounds and assign the correct RT to each target. Manual integrations at this point do not have to be documented and must not be included in the calibration evaluation.

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5.1.3 Reprocess the data and confirm that all of the targets can be identified and properly integrated. If the targets cannot be identified and properly integrated, adjust the integration parameters and reprocess the data. This is an important step. If the data system cannot reliably detect and integrate the targets in the mid-level standard, the probability of properly identifying and quantifying the targets in the remaining standards and samples are low.

5.1.4 Process the remaining calibration standards and confirm that the data system can routinely and properly identify the target compounds at each calibration level. Pay particular attention to the lowest level standard because this standard typically defines the reporting limit (RL). The integration parameters should allow for detection of the target compounds down to the quantitation limit or reporting limit.

5.1.5 The integration parameters set at the initial calibration must remain in use until the next calibration is performed, except as noted in 4.3. Manual integrations are used only when the conditions listed in Section 3.0 are encountered. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system.

5.1.6 Any manual integration of a chromatographic peak or group of peaks must be documented. In all instances where the data system report has been edited or where manual integration has been performed, the chromatographic system operator must clearly identify such edits or manual procedures as listed below:

- Manual integrations indicated on expanded scale "after" chromatograms.
- Re-integration technique marked, if available, on the data system
- Technical justification for manual integration.
- Analyst's initials and date. (data system application of analyst name or initials is acceptable so long as the data system allows the analyst to log in as himself or herself and has password control)

5.1.7 Project specific, client, program or STL laboratory specific requirements for manual integration may exceed the requirements of this policy. In those instances, the more specific requirements will apply or written approval allowing a deviation from the requirement must be received. For example:

- Requiring the before and after printing of the chromatograms
- Handwritten or electronic initialing and dating the changes made to the report
- Hardcopy printout of the EICP of the quantitation ion displaying the manual integration included in the raw data for all standards and samples, this applies to internal standards and surrogates as well.
- Requiring manual integrations to be documented in the project or case narrative

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5.2 Data reviewers shall confirm that documentation of manual integration is complete and that each manual integration is appropriate. This inspection shall be documented. At a minimum, the information required in Section 5.1.6 must be reviewed.

5.3 If integration indicates problems with analytical instrumentation, investigate the problem and take action to correct it. If poor chromatography routinely interferes with the ability to identify and quantify components; is a result of delayed system maintenance; and is not inherent in the system, such as (benzoic acid for Method 8270; benzo(b)anthracene and benzo(k)anthracene merging with column age; and dichlorobutenes merging with column age), then instrument maintenance must be performed. If instrument and data conditions have changed such that the default integration parameters no longer work as effectively, it is acceptable to change the default parameters and reprocess all affected data, including the associated standards, lab QC, and field samples, using the new integration parameters. Further manual manipulations after this reprocessing must be treated as manual integrations. The reason for reprocessing must be documented and approved.

5.4 Manual integrations on some data systems (e.g., Multichrom) may consist of adjusting integration parameters on a by-sample basis. Changes such as these must be documented.

5.5 Any deficiencies must be resolved with the analyst or their supervisor before the results are approved and released from the analytical department. Any questions arising from review of the documentation must be investigated in the electronic record, when available, prior to data acceptance. Any failures to complete these requirements shall be described in a non-conformance report.

5.6 Any concerns about violations of this policy must be reported to the facility Quality Manager, Laboratory Director or the Corporate Quality Director.

5.7 Electronic data surveillance is performed using *Mint Miner*™ Software. This software allows the user to connect to a workstation or archived data source and evaluate the audit trails in the electronic data file (refer to WI-STL-002/A-08/03).

6.0 DEFINITIONS

- Integration: The determination of the area or height under a curve (peak).

- Manual integrations: Include any adjustments to measurements of analytical peaks not applied equally to all applicable samples and QC parameters in an analytical batch by the data acquisition system. For the purpose of this policy, a manual integration has been performed if results for any of the analyses could not be duplicated by another analyst using the indicated calibration and standard peak integration protocol. Manual adjustments to peaks can include baseline changes, retention time window adjustments, changes to peak identification in samples (calibration standards' changes as required are exempt), manual peak height measurements, or changes to the formula used to

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model analytical peak areas or changes to background subtraction algorithms for GC/MS tuning. Although the latest analytical instruments are equipped to perform automatic integrations, manual integrations are sometimes necessary to accurately analyze samples if peaks are poorly resolved, exhibit tailing, the baseline drifts or is noisy, or other similar situations.

- Chromatograms: In the context of this policy, chromatograms are not necessarily limited to the output of chromatography instruments or automated data systems. They can include strip charts, integrator printouts, computer screen dumps, or any graphic display of a continuous signal from an analytical detector.

- Chromatography: A separation technique involving differential retention of components between stationary and mobile phases.

- Baseline: The chromatographic signal plotted as a function of time in the absence of signal construction from components of interest.

- Peak: An increase in signal from baseline to a maximum and then back to baseline.

- Coelution: the concurrent elution of two or more compounds to the detector at the same time.

- Elution: The process of movement of compounds from the chromatographic system.

- "Wavy" Baselines: A "wavy" baseline can be caused by minor impurities in carrier gas or solvent.

- Negative Spikes: Negative spikes in chromatograms are sudden upsets in chromatographic signal below the normal baseline.

- Sudden Rise in Baseline: A rise in the baseline is caused by several factors including high concentration of components in the sample and by normal column bleed.

- Carry-over: Carry over results from system contamination from previous analyses and results in signal unrelated to the current analysis.

- Peak Tailing: Peak tailing is a delayed return of a peak to chromatographic baseline and could be related to a delay of compound elution from the chromatographic system by adsorption or dead volume effects.

- Interference Peaks or Fused Peaks: Peaks that partially or totally coelute with the peak of interest.

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7.0 APPENDICES

- Appendix I. Examples of Peak shape and Proper integration Documenting Manual Integrations
- Appendix II. Examples of Improper Integration and Inflection Point Guidance

8.0 TRAINING MODULE

- Acceptable Manual Integration Practices, September 2004, Version 1.1: T-Q-004.

9.0 REVISION HISTORY

- Revision 1; dated 12/1/01
- Revision 2; Amended Section 5.7; dated 9/17/04.

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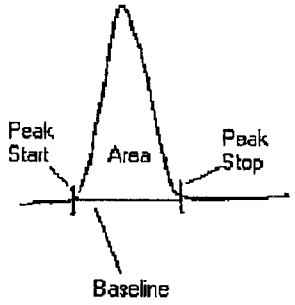
Appendix I.

Examples of Peak shape and Proper integration Documenting Manual Integrations

Ideal peak (Gaussian Shape) The start of integration is where the peak begins to rise from the background, and the end is where the peak returns to background.	
Tailing Peak Tailing peaks result from surface adsorption effects or dead volume in the instrument. When integrating tailing peaks, include only and all area that can be attributed to compound. If the baseline rises, the integration line should rise with the baseline.	

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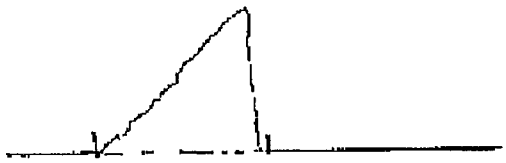
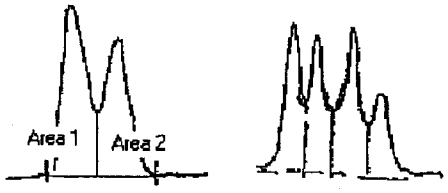
Fronting Peak Fronting peaks generally result from column overload and/or overcapacity. An example is benzoic acid on a 5% phenyl phase. In some cases, it is inherent in the analysis, in others, it is indicative of problems in the system. The analyst must have knowledge of their system. To integrate these peaks, it is important to have prior knowledge of how the compound acts when overloading versus co-eluting with a contaminate peak.	
Fused Peaks Fused peaks are near coeluters with some separation. They will occur in calibration mixes as well as real samples. To integrate, split the components with a vertical drop from the valley to the baseline.	
Hydrocarbon Envelope For semivolatile hydrocarbon analysis, most fuels produce "humpograms" like this one. Integration shall be performed in accordance with method, program or client specific requirements.	
Peak on a Baseline Rise Aside from hydrocarbon analysis, which uses the total area within a window for quantitation, baseline variations are not integrated. Therefore, skim the baseline rise to integrate the peak properly.	

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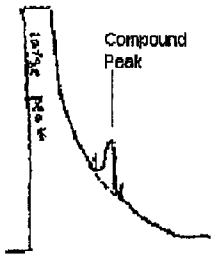
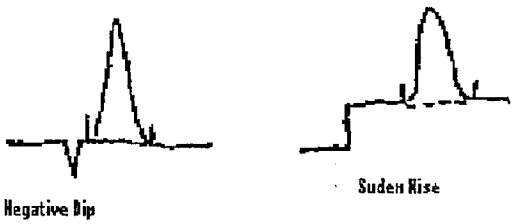
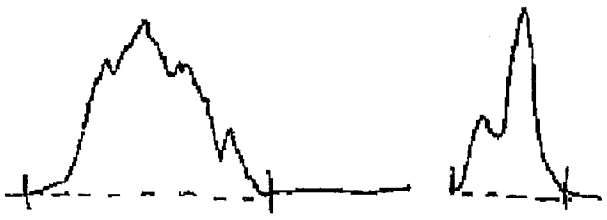
Skimmed Peak Use the tangent skimming functions of the integration software to correctly integrate small peaks on the tails of big peaks. Dropping vertical integration lines to the baseline of the big peak adds extra area which is not a part of the small peak, and results in high bias.	
Peak near a baseline upset Negative dips are common in ECD analysis, and the sudden rises in baseline are common with programmable fluorescence detectors where gain/wavelength switching occurs. Often, the default integration will go from the base of the negative peak to the far side of the peak of interest. This is results in high bias and is incorrect. Similarly, a default integration using the low part of the baseline rise and the far side of the peak of interest will also result in high bias and must be corrected.	
Split Peak Particularly in GC/MS analysis, low-level peaks may appear jagged or split. To integrate these properly, the analyst must have prior knowledge of the peak/compound chromatography.	

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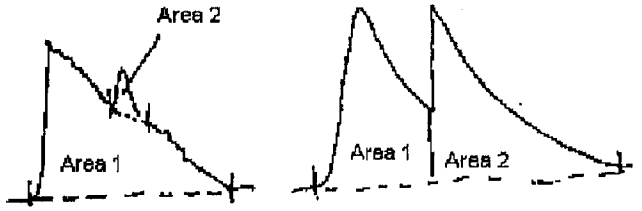
Fused tailing peaks These are very difficult to accurately quantify. It is best to do maintenance on the chromatography system to avoid this situation. To integrate these properly, the analyst should have prior knowledge of the compounds of interest. It is important to be consistent when integrating standards and samples.	

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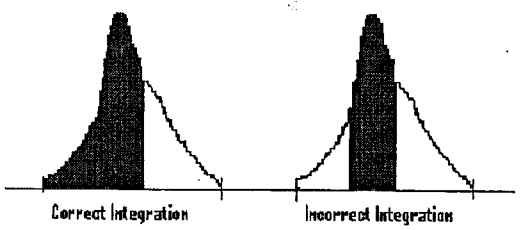
Appendix II.

Examples of Improper Integration and Inflection Point Guidance

An inflection point must be apparent when and if an integration point is drawn. For example:



When MS data has an inflection point in a peak, as shown in the example above, checking the underlying spectrum may be necessary to correctly manually integrate. On some chromatographic columns, for example, allyl chloride and carbon disulfide elute very close to each other, and they both share the primary characteristic ion mass 76. For both compounds mass 76 is the quantification mass. If two compounds can not be separated and a fused peak is going to be split at the inflection point, this can be correctly verified by looking at the spectra for each scan. In this example, the 76 peak may be fused, but the secondary ions will indicate which compound is present (carbon disulfide with secondary ion 78 and allyl chloride with secondary ions 41, 39 and 78).

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STL Chicago
Explosives Case Narrative

[redacted]

Job #: 236546-1 through 12
Explosives

1. STL Chicago used the following HPLC systems for analysis of Nitroaromatics and Nitramines:

ID#	INSTRUMENT	COLUMN TYPE	DETECTOR
43	Agilent 1100	C18 (Primary)	UV - 254nm
44	Agilent 1100	Phenyl Hexyl (Confirmation)	UV - 254nm

2. These samples were extracted and analyzed for explosives based on SW846 method 8330.

3. All required hold times were met for the extraction and analysis.

4. The method blank was below the reporting limit for all target compounds.

5. The surrogate compound used for this analysis was 1,2-Dinitrobenzene (1,2-DNB). All surrogate recoveries were within required control limits except those that were diluted out and flagged "D". Surrogate recoveries for samples 236546-6 (1/10), -7 (1/10), and –10 were reported from the confirmation column due to interference.

6. All blank spike recoveries were within required control limits.

7. All MRL checks were within the required limits of 70%-130%.

8. A matrix spike and a matrix spike duplicate were performed on sample 236546-3 (COP-4-GWMW05A-05). All matrix spike and matrix spike duplicate recoveries and RPDs were within required control limits except RPD for RDX was 36%.

9. All initial and continuing standard calibrations associated with these samples were in control on the primary (C18) column. All SSV recoveries were within control limits of 85%-115%.

10. All initial and continuing standard calibrations associated with these samples were in control on the confirmation (Phenyl Hexyl) column for all compounds needing confirmed. All SSV recoveries were within control limits of 85%-115%.

11. Target compounds were confirmed using a second column (Phenyl Hexyl). Most target compounds detected were <40% difference between columns. See Form 10s for further details.

=7 12. All manual integrations were performed following the laboratory's Manual Integration SOP. The reason for each manual integration was documented and reviewed. All manual integrations are identified as M1 (missed peak), M2 (mis-identified peak), M3 (poor baseline), M4 (peak not integrated correctly by data system) or M5 (other). ICAL points, QC samples, or CCVs did not require any manual integration. However, some samples required manual integration and are included in package.

Patti Gibson

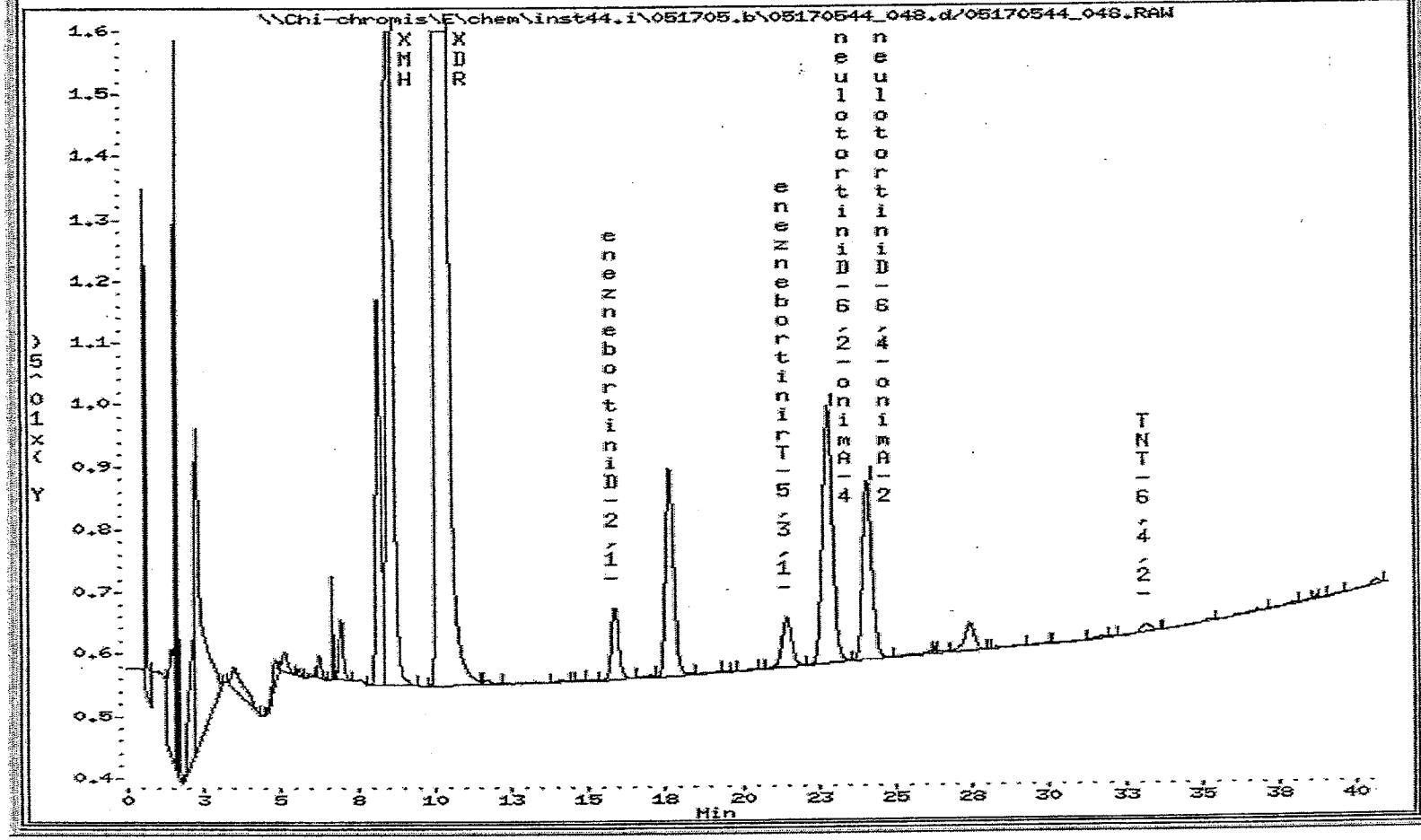
Patti Gibson
Organics Section Manager

5/25/05
Date

Graphic Report Host: CHI-ANGEL

Data File: \\Chi-chromis\E\chem\inst44.i\051705.b\05170544_048.d
Page 1
Date : 19-MAY-2005 11:56
Client ID: COP-4-GWMW07A-05
Instrument: inst44.i
Sample Info: 051705,expl44,236546-7
Volume Injected (uL): 100.0
Operator: newkirks
Column phase: Phenyl Hexyl
Column diameter: 4.60

Exit
Prev
Next
Print



STL Chicago

SW846 Method 8330

Data file : \\CHI-Chromis\E\chem\inst44.i\051705.b\05170544_048.d
Lab Smp Id: 236546-7 Client Smp ID: COP=4-GWMW07A-05
Inj Date : 19-MAY-2005 11:56
Operator : newkirks Inst ID: inst44.i
Smp Info : 051705,exp144,236546-7
Misc Info : dc=
Comment : HP 1100 Series HPLC HP 1100 UV Det
Method : \\CHI-CHROMIS\E\chem\inst44.i\051705.b\exp144.m
Meth Date : 20-May-2005 14:03 newkirks Quant Type: ESTD
Cal Date : 05-MAY-2005 04:18 Cal File: 05040544_006.d
Als bottle: 48
Dil Factor: 1.00000
Integrator: HP Genie Compound Sublist: 8330rout.sub
Target Version: 4.04
Processing Host: CHI-GROUPER

Concentration Formula: Amt * DF * Uf * Vt/(Vo * Vi)

Name	Value	Description
DF	1.000	Dilution Factor
Uf	100.000	Correction factor
Vt	6000.000	Volume of final extract (uL)
Vo	770.000	Volume of sample extracted (mL)
Vi	100.000	Volume injected (uL)

	Compounds	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/ul)	CONCENTRATIONS FINAL (ug/L)
	1 MNX	Compound Not Detected.					
	2 HMX	8.580	8.592	-0.012	256538	4.61893	35.992(A) E
	3 RDX	10.358	10.249	0.109	97458	14.9435	116.44(AM) E
	4 Nitrobenzene	Compound Not Detected.					
$	5 1,2-Dinitrobenzene	15.877	15.878	-0.001	11492	0.16852	1.313 PA 5/25/05
	6 1,3-Dinitrobenzene	Compound Not Detected.					
	7 2-Nitrotoluene	Compound Not Detected.					
	8 4-Nitrotoluene	Compound Not Detected.					
	9 1,3,5-Trinitrobenzene	21.467	21.480	-0.013	7964	0.08803	0.6860
	10 3 Nitrotoluene	Compound Not Detected.					
	11 4-Amino-2,6-Dinitrotoluene	22.816	22.811	0.005	41369	0.66043	5.146
	12 2-Amino-4,6-Dinitrotoluene	24.090	24.091	-0.001	28890	0.34574	2.694
	13 2,6-Dinitrotoluene	Compound Not Detected.					
	14 2,4-Dinitrotoluene	Compound Not Detected.					

SAP 5/20/05

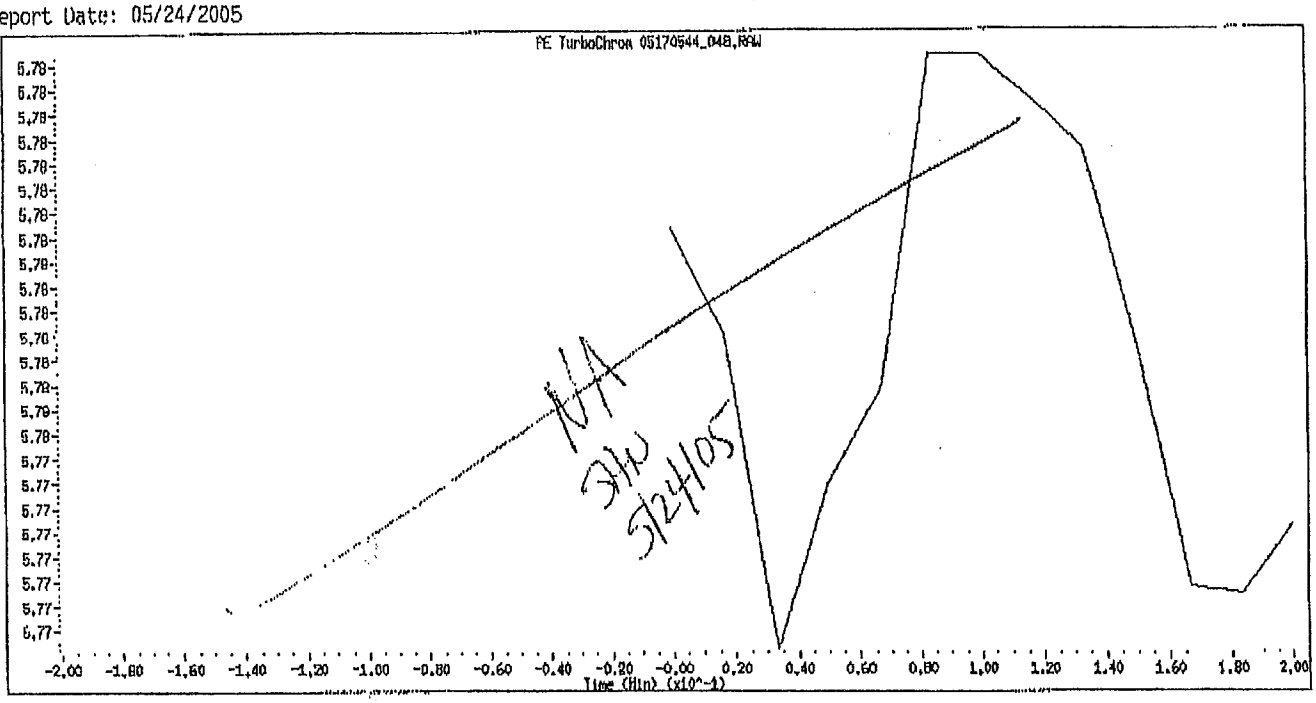
Compounds	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/ul)	CONCENTRATIONS FINAL (ug/L)
15 2,4,6-TNT	33.178	33.195	-0.017	1353	0.01619	0.1262(a)
16 Tetryl	Compound Not Detected.					

QC Flag Legend

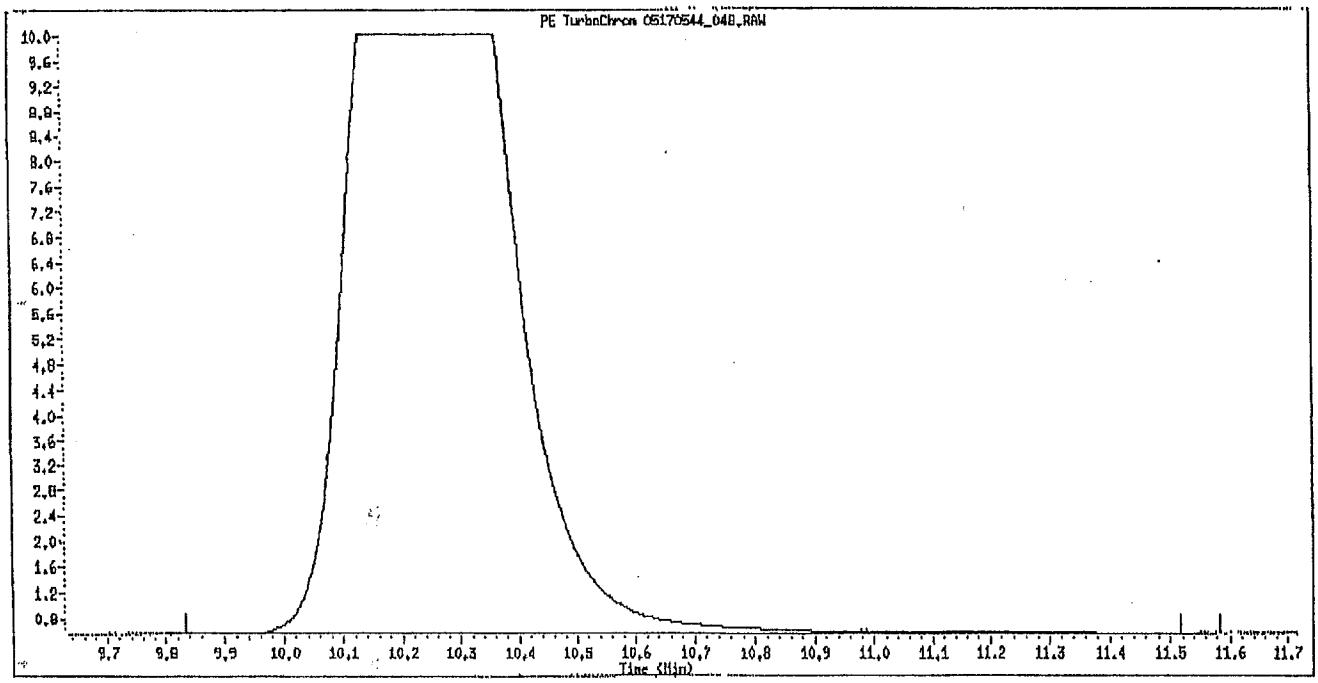
a - Target compound detected but, quantitated amount Below Limit Of Quantitation(BLOQ).
A - Target compound detected but, quantitated amount exceeded maximum amount.
M - Compound response manually integrated.

SDG 5/20/05

Data File Name: 05170544_048.d
Inj. Date and Time: 19-MAY-2005 11:56
Instrument ID: inst44.i
Client ID: COP-4-GWMW0/A-05
Compound Name: RDX
CAS #:
Report Date: 05/24/2005



Original Integration



Manual Integration

Manually Integrated By: NewkirkS
Manual Integration Reason: Peak missed by data system

5/25/05

STL Chicago
STANDARD OPERATING PRACTICE (SOP) CHANGE FORM

Original SOP Number/Revision #: UMB-8270 Rev 14 Last Mod ID (circle): NA/A
SOP Title: Gas Chromatography/Mass Spectrometry-Semi-Volatiles SW-846 Method 8270
Affected SOP Section Number(s): 8.2.9
Effective Date: 8/2/6

CONTROLLED DISTRIBUTION

COPY # :
ISSUED TO : **Uncontrolled**

Full Signature Approvals Are Kept on File with Severn Trent Laboratories Standard Practice Records

Revision Number with Mod ID:

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. **Append this form to the front of the SOP copy.**

1. Reason for SOP Change: Update of policy of internal standard recoveries in samples.

2. Summary of Procedure Change (circle to indicate if there are attachments to this form: (No) Yes: # pages attached = _)

8.2.9 Internal Standard Areas / Retention Times Corrective Action Policy

The internal standard areas in any sample analysis will not vary by more than a factor of two (-50% to +100%) from the internal standard areas in the corresponding initial calibration mid-point of the HSL (default list) calibration. Some QAPPs require (-50% to +100%) from the internal standard areas in the calibration verification standard. QAPP requirements will supersede the SOP policy. The internal standards in the samples will not vary in retention time by more than ±30 seconds from the internal standard retention times in the corresponding calibration verification standard (most AFCEE/LCG/DOD clients require ± 30 seconds from the internal standard retention times in the corresponding initial calibration mid-point of the HSL (default list) calibration). Upon the identification of an out-of-control event in a sample analysis (in regards to internal standard areas or retention times), the corrective action is documented on the Sample CAR with the decision whether to reanalyze the sample, initialed and dated.

x [signature] 8/2/6
Initiated/Reviewed By: Name/Date

N/A
Initiated/Reviewed By: Name/Date

x [signature] 8/1/06
Approval Signature/Date: Section Manager

[signature] 08-02-06
Approval Signature/Date: QA Manager or Designee

STL CHICAGO
LABORATORY STANDARD OPERATING PROCEDURE

SOP No.	Revision No.	Date	Page
UMB-8270	14	11/07/05	1 of 66

TITLE: Gas Chromatography / Mass Spectrometry - Semi-Volatiles SW-846 Method 8270

Updated by:	Signature:	Date
Gary L. Rynkar Section Manager, GC/MS Dept.	Gary L. Rynkar	11/7/5

Approved by:	Signature:	Date
Gary L. Rynkar Section Manager, GC/MS Dept.	Gary L. Rynkar	11/7/5
David W. Mazur Env. Health & Safety Coor.	David W. Mazur	11/10/05
Terese A. Preston Quality Manager	Terese A. Preston	11/7/05

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) outlines the guidelines for the analysis of semi-volatile base/neutral and acid (BNA) compounds by Gas Chromatography/Mass Spectrometry (GC/MS). This SOP was written using SW-846 3rd Edition, Methods 8270A, 8270C and 8000B as references.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

Specific requirements pertaining to the DOD QSM Version 3.0 are located in Appendix A. These requirements are additionally applicable to all NFESC projects. Any deviations from these procedures and/or variances from must be addressed appropriately in accordance with standard operating protocol and pre-approved on a project by project basis.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Reporting Limits

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are ~3-5x the respective MDL to ensure confidence in the value reported.

Reporting limits [a.k.a., Practical Quantitation Limits (PQLs)] are assessed annually based on MDL performance. If the MDL does not meet the routine laboratory reporting limit or the method specified limit, it is repeated, or the laboratory reporting limit is reassessed. Table 1 defines the laboratory's reporting limits for each compound that can be routinely analyzed by this method according to each matrix.

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.2 Summary of Methods

This method is appropriate for the analysis of BNA's in wastewaters, soils, sediments, solids, sludges, wastes, and oils. Concentrated extracts are transferred to crimp-top vials, internal standard solution added, with subsequent analysis on the GC/MS. The method finds applicability for most BNA compounds that are soluble in dichloromethane (DCM, a.k.a., Methylene chloride) and chromatograph well on a fused-silica capillary column. Table 2 lists those compounds with their characteristic ions. The approximate retention times were generated by a specific GC/MS system.

The following exceptions are noted: Benzidine is subject to loss during solvent concentration and chromatographs poorly. Hexachlorocyclopentadiene is subject to decomposition in the inlet, chemical reaction in acetone and photochemical decomposition. N-nitrosodimethylamine can be difficult to separate from the solvent front. N-nitrosodiphenylamine decomposes in the injection port and cannot be separated from diphenylamine. Other qualitative procedures are listed in EPA Method 625 for these compounds.

Those samples suspected of high background levels are screened by a GC/MS prior to analysis. Initial dilutions are determined from this screen.

Instrument calibration occurs prior to analysis and every 12 hours of run-time. Instrument maintenance is performed as needed, on a daily, monthly or yearly basis, as the specific action requires.

2.0 INTERFERENCES

External interference's can be caused by contaminants from sample containers, preparative glassware and reagents, inlet liners, syringes and columns and manifest themselves in discrete peaks and/or elevated baselines. "Soap" peaks and phthalates are the most common external interferences encountered. Proper glassware preparation, sample handling, and instrument maintenance should reduce the contamination from these sources. A laboratory reagent blank is analyzed with each batch to demonstrate the absence of these contaminants.

Rinsing the syringes well, both the syringe used for sample prep and sample injection, prior to and after use, for each sample or standard is critical. Assigning separate functions to the syringes prevents cross-contamination (introduction of compounds from one sample to a sample not originally containing those compounds). Replacing the rinse and DCM dilution containers often is also necessary.

Carryover is another source of contamination. After analysis of highly concentrated samples or background containing samples, a DCM blank should be run, or at a minimum, the oven temperature should be raised to 300°C and baked out.

Internal or matrix interference's can be co-extracted from the sample during preparation. These can appear as large distinct peaks and/or elevated baselines. Occasionally, matrix interferences manifest themselves as low/high recoveries of spike compounds. Matrix interferences vary from sample to sample. Unless specifically requested by the client, clean-up procedures are not performed to remove heavy background or interferences.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

- The GC/MS contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.
- The mass spectrometer is under deep vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.
- There are areas of high voltage in both the GC and the MS. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: **This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride (DCM)	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

4.1 GC/MSD

A temperature-programmable GC is equipped with a splitless injection port and accessories (syringes, gases, and columns). The column used is a DB5MS, 30m x 0.25mm ID or equivalent bonded-phase silicone coated fused-silica capillary column, with 0.25um film thickness. Interfaced with a mass-selective detector capable of scanning from 35 to 500 amu every second or less using 70 volts electron energy in the Electron Ionization (EI) mode. The system must be able to produce an acceptable mass spectrum of decafluorotriphenylphosphate (DFTPP) when 50-ng is injected on the column.

4.2 Data System

The analytical system is interfaced with a data system capable of continuing acquisition and storage of mass spectral data. The software allows plotting of specific masses versus time or scan numbers (Extracted Ion Current Profile - EICP) and integration of that abundance. The system also contains the latest NBS Library.

4.3 Accessories

- 10 uL, 25 uL, 500 uL, 1000 uL and 2500 uL gas-tight syringes.
- Amber and clear vials (1.5 mL and 4.5 mL)
- Teflon/silicone septa
- Crimp-top and screw-top vial caps

4.4 Current Hardware/Software

- 3 – 5890 Series II Plus Gas Chromatographs with Electronic Pressure Control (EPC), Hewlett-Packard (HP)
- 3 – 6890N Gas Chromatograph with Electronic Pressure Control (EPC), Agilent
- 3 – 5973 Mass Selective Detectors, Agilent
- 3 – 5972 Mass Selective Detectors, Hewlett-Packard
- 3 – 7683 Autosampler and Accessories, Agilent
- 3 – 7673 Autosamplers and Accessories, Hewlett-Packard
- 6 – Hewlett-Packard ChemStations B.02.04 software and peripheral hardware
- 1 – Hewlett-Packard Chemserver with Target 3.5.

5.0 REAGENTS AND STANDARDS

All neat standards or stock solutions received are entered into the laboratory's LIMS (LabNet). A standard label is printed from LabNet and affixed to the bottle or ampule. All standards are then stored at -10°C to -20°C until needed. All glassware and syringes needed to prepare reagents and standards must be cleaned, dried and rinsed well with the solvent to be used (methanol and DCM).

All information concerning standard preparation must be entered into LabNet. The labels contain the following information: Standard ID, solution description (content, weights, concentrations, date prepared, expiration date and analyst initials). All neat standards (referenced by standard type and date in LabNet) used in preparations are noted and cross-referenced here, providing a standard tracking mechanism. The expiration date of any prepared standard cannot exceed the expiration date assigned for any neat standard that is a component in the prepared standard mixture.

5.1 Surrogate Parent Spiking Solution

The surrogate spiking solution is obtained from Cerilliant as a prepared solution in a 100 mL amber glass Teflon-lined screw-capped bottle. The surrogate spike is prepared by Cerilliant using EPA certified standards at the following concentrations:

Compound	Concentration (ug/mL)
p-Terphenyl-d_{14}	1000
Nitrobenzene-d_5	1000
2-Fluorobiphenyl	1000
Phenol-d_5	1500
2-Fluorophenol	1500
2,4,6-Tribromophenol	1500

- Life of Standard: 6-months from date of transfer of standard or less as indicated by the manufacturers expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

5.1.1 Surrogate Working Spike Solution

10 mLs of surrogate stock + 90 mLs MeOH in a 100 mL amber glass Teflon-lined screw-capped bottle. The working surrogate spike is prepared by the extractions department at the following concentrations:

Compound	Concentration (ug/mL)
p-Terphenyl-d_{14}	100
Nitrobenzene-d_5	100
2-Fluorobiphenyl	100
Phenol-d_5	150
2-Fluorophenol	150
2,4,6-Tribromophenol	150

- Life of Standard: 6-months from date of transfer of standard or less as indicated by the manufacturers expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

The surrogate spike solution is spiked in all samples, the matrix spike/matrix spike duplicate (MS/MSD) samples, method blanks (MB), and the laboratory control sample (LCS) at a volume of 0.5 mLs prior to extraction. This results in a spiking level of 75 ug for the Acid surrogate compounds and 50 ug for the Base/Neutral surrogate compounds.

5.1.2 Surrogate Working Spike Solution – HP 5973 Instruments

5 mLs of surrogate stock + 95 mLs MeOH in a 100 mL amber glass Teflon-lined screw-capped bottle. The working surrogate spike is prepared by the extractions department at the following concentrations:

Compound	Concentration (ug/mL)
p-Terphenyl-d_{14}	50
Nitrobenzene-d_5	50
2-Fluorobiphenyl	50
Phenol-d_5	75
2-Fluorophenol	75
2,4,6-Tribromophenol	75

- Life of Standard: 6-months from date of transfer of standard or less as indicated by the manufacturers expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

The surrogate spike solution is spiked in all samples, the matrix spike/matrix spike duplicate (MS/MSD) samples, method blanks (MB), and the laboratory control sample (LCS) at a volume of 0.5 mLs prior to extraction. This results in a spiking level of 37.5 ug for the Acid surrogate compounds and 25 ug for the Base/Neutral surrogate compounds.

5.2 LCS and Matrix Spike Parent Solution

The full list spike solution is prepared by the extractions department from stock solutions. The parent spiking solutions are prepared from stock solutions from Cerilliant using EPA certified standards at the following concentrations:

5.2.1 8270 LCS Mix Parent

The 8270 LCS Mix Calibration Stock is purchased from Cerilliant at a 200 ug/mL concentration with 5 mLs volume.

Acenaphthene	1,2-Dichlorobenzene	2-methylphenol (o-Cresol)
Acenaphthylene	1,3-Dichlorobenzene	4-methylphenol (p-Cresol)
Acetophenone	1,4-Dichlorobenzene	Naphthalene
Aniline	3,3-Dichlorobenzidine	2-Nitroaniline
Anthracene	2,4-Dichlorophenol	3-Nitroaniline
Azobenzene	2,6-Dichlorophenol	4-Nitroaniline
Benzo(a)anthracene	Diethylphthalate	Nitrobenzene
Benzidine	2,4-Dimethylphenol	2-Nitrophenol
Benzo(b)fluoranthene	Dimethylphthalate	4-Nitrophenol
Benzo(k)fluoranthene	Di-n-butylphthalate	N-Nitroso-di-n-butylamine
Benzo(g,h,i)perylene	2,4-Dinitrophenol	N-Nitrosodiethylamine
Benzo(a)pyrene	2,4-Dinitrotoluene	N-Nitrosodimethylamine
Benzoic acid	2,6-Dinitrotoluene	N-Nitroso-di-n-propylamine
Benzyl alcohol	Dinoseb	N-Nitrosodiphenylamine
Biphenyl	Di-n-octylphthalate	N-Nitrosomethylethylamine
bis(2-Chloroethoxy)methane	1,4-Dioxane	N-Nitrosopiperidine
bis(2-Chloroethyl)ether	Diphenyl ether	N-Nitrosopyrrolidine
Bis(2-Chloroisopropyl)ether	2-Ethoxyethanol	Pentachlorobenzene
bis(2-Ethylhexyl)phthalate	Fluoranthene	Pentachloroethane
4-Bromophenylphenylether	Fluorene	Pentachlorophenol
Butylbenzylphthalate	Hexachlorobenzene	Phenanthrene
Carbazole	Hexachloro-1,2-butadiene	Phenol
p-Chloroaniline	Hexachlorocylcopentadiene	Pyrene
4-Chloro-3-methylphenol	Hexachloroethane	Pyridine
2-Chloronaphthalene	Hexachlorophene	1,2,4,5-Tetrachlorobenzene
2-Chlorophenol	Hexachloropropene	2,3,4,6-Tetrachlorophenol
4-Chlorophenylphenylether	Indeno(1,2,3-c,d)pyrene	1,2,4-Trichlorobenzene
Chrysene	Isophorone	2,4,5-Trichlorophenol
Dibenz(a,h)anthracene	4,6-Dinitro-2-methylphenol	2,4,6-Trichlorophenol
Dibenzofuran	2-Methylnaphthalene	

- Life of Standard: 12-months or less as indicated by the manufacturers expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

5.2.2 8270 LCS 3,3'-Dimethylbenzidine Parent

The 8270 LCS 3,3'-Dimethylbenzidine Parent Stock is purchased from Cerilliant at a 2,000 ug/mL concentration with 1 mL volume.

3,3'-Dimethylbenzidine

- Life of Standard: 12-months or less as indicated by the manufacturers expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

5.2.3 LCS and MS Working Spike Solution

50 mLs of 8270 LCS Mix Parent Stock + 5 mLs of 8270 LCS 3,3'-Dimethylbenzidine Parent Stock are brought to a 100 mL final volume with DCM. This results in a spiking solution of 8270 HSL compounds at 50 ug/mL. This is stored in a 100 mL labeled amber, screw top vial with Teflon lined septum, at -10 to -20°C until needed. All preparation information is recorded in LabNet and assigned a LabNet ID Number. An expiration date is assigned for 6-months from date of preparation or less as indicated by the manufacturer.

The spiking solution is spiked in all LCS and MS/MSD samples at a volume of 1.0 mL prior to extraction. This results in a spiking level of 50 ug/mL for all compounds.

5.2.4 SSV(IcalSpike) Spike Solution

The SSV (IcalSpike) solution is prepared from a stock solution purchased from Supelco (100 ug/mL) to result in a spike level of 50 ug/mL, for most compounds. Only the routinely analyzed 8270C compounds are present in the spike.

5.3 DFTPP / DDT / Pentachlorophenol (PCP) / Benzidine Stock Solutions

The DFTPP/DDT stock is purchased from Supelco at 1000 ug/mL; the PCP stock is purchased from Supelco at 5000 ug/mL; and the Benzidine stock is purchased through Supelco at 1000 ug/mL. All stocks are transferred to amber-glass, screw-topped, Teflon lined vials; assigned a LabNet ID Number; and documented in LabNet. Stock standards are stored at -10° to -20°C. An expiration date is assigned for 1-year from date of transfer or less as indicated by the manufacturer.

5.3.1 DFTPP / DDT / PCP / Benzidine Parent Solution

250 uLs of DFTPP/DDT stock + 50 uLs of PCP stock + 500 uL of Benzidine stock are brought to a 1000 uL final volume with DCM. This results in a parent solution of DFTPP/DDT/PCP at 250 ug/mL and Benzidine at 500 ug/mL. This is stored in a 1.5 mL labeled amber, screw top; vial with Teflon lined septum, at -10 to -20°C until needed. All preparation information is recorded in LabNet and assigned a LabNet ID Number. An expiration date is assigned for 6 months from date of preparation or less as indicated by the manufacturer.

5.3.2 The DFTPP / DDT / PCP / Benzidine Working Solution

100 uLs of the DFTPP/DDT/PCP/Benzidine Parent Solution are added to 900 uLs of DCM, resulting in a concentration of 50 ng/uL DFTPP/DDT/PCP and 100 ng/uL Benzidine. This is stored in a 1.5 mL labeled amber, crimp-top, autosampler vial, at -10 to -20°C until needed. All preparation information is recorded in LabNet and assigned a LabNet ID Number. An expiration date is assigned for 6-months from date of preparation or less as indicated by the manufacturer. Alternately, DFTPP/DDT can be spiked at the same concentration in the calibration verification solution.

5.4 Internal Standard Solution

This solution is obtained as a mixture from Cerilliant:

Internal Standards (4,000 ug/mL)	
1,4-Dichlorobenzene- d_4	Phenanthrene- d_{10}
Naphthalene- d_8	Chrysene-d_{12}
Acenaphthene- d_{10}	Perylene- d_{12}

Once the 1.0 mL ampule is opened, the entire contents are transferred to a 1.5-mL amber gas-tight conical vial and labeled appropriately. All preparation procedures are recorded in LabNet. Unopened ampules can be kept for the period indicated by the manufacturer, and are stored at -10° to -20°C until needed.

Refer to Table 3 for a listing of Internal Standards and corresponding ions assigned for quantitation.

- Life of Standard: 12-months or less as indicated by the manufacturers expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

5.4.1 Internal Standard Working Solution – HP 5973 Instruments

600 uLs of the Internal Standard Solution are added to 2400 uLs of DCM, resulting in a concentration of 800 ng/uL of Internal Standard. The entire contents are kept in a 3.0-mL amber gas-tight conical vial and labeled appropriately. All preparation procedures are recorded in LabNet. The vials are stored at -10° to -20°C until needed.

- Life of Standard: 6-months or less as indicated by the manufacturer's expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

5.5 Initial Calibration Standards

5.5.1 Hazardous Substance List (HSL) Stock Standards

The parent initial calibration solutions are prepared from stock solutions from Cerilliant using EPA certified standards at the following concentrations:

5.5.1.1 8270 BNA Working Calibration Standard

The 8270 BNA Working Calibration Standard Stock is purchased from Cerilliant at a 160 ug/mL concentration (except where noted) with a 1.0 mL volume.

Acenaphthene	Diethylphthalate	2-Nitroaniline
Acenaphthylene	p-Dimethylaminoazobenzene	3-Nitroaniline
Acetophenone	7,12-Dimethylbenz(a)anthracene	4-Nitroaniline
2-Acetylaminofluorene	3,3-Dimethylbenzidine	Nitrobenzene
4-Aminobiphenyl	2,4-Dimethylphenol	2-Nitrophenol
Aniline	Dimethylphthalate	4-Nitrophenol
Anthracene	1,3-Dinitrobenzene	N-Nitroso-di-n-butylamine
Azobenzene	2,4-Dinitrophenol	N-Nitrosodiethylamine
Benzo(a)anthracene	2,4-Dinitrotoluene	N-Nitrosodimethylamine
Benzidine	2,6-Dinitrotoluene	N-Nitroso-di-n-propylamine
Benzo(b)fluoranthene	Dinoseb	N-Nitrosomethylethylamine
Benzo(k)fluoranthene	Di-n-octyl phthalate	N-Nitrosopiperidine
Benzo(g,h,i)perylene	Diphenylamine	N-Nitrosopyrrolidine
Benzo(a)pyrene	Ethylmethanesulfonate	5-Nitro-o-toluidine
Benzyl alcohol	Fluoranthene	Pentachlorobenzene
bis(2-Chloroethoxy)methane	Fluorene	Pentachloroethane
bis(2-Chloroethyl)ether	Hexachlorobenzene	Pentachloronitrobenzene
bis(2-Chloroisopropyl)ether	Hexachloro-1,3-butadiene	Pentachlorophenol
bis(2-ethylhexyl)phthalate	Hexachlorocylcopentadiene	Phenacetin
4-Bromophenylphenylether	Hexachloroethane	Phenanthrene
Butylbenzylphthalate	Hexachlorophene	Phenol
Carbazole	Hexachloropropene	2-Picoline
p-Chloroaniline	Indeno(1,2,3-c,d)pyrene	Pronamide
Chlorobenzilate	Isodrin	Pyrene
4-Chloro-3-methylphenol	Isophorone	Pyridine
2-Chloronaphthalene	Isosafrole	Safrole
2-Chlorophenol	Kepone	1,2,4,5-Tetrachlorobenzene
4-Chlorophenylphenylether	2-Methylcholanthrene	2,3,4,6-Tetrachlorophenol
Chrysene	4,6-Dinitro-2-methylphenol	o-Toluidine
Diallate	Methylmethanesulfonate	1,2,4-Trichlorobenzene
Dibenz(a,h)anthracene	2-Methylnaphthalene	2,4,5-Trichlorophenol
Dibenzofuran	2-methylphenol (o-Cresol)	2,4,6-Trichlorophenol
Di-n-butylphthalate	3-methylphenol (m-Cresol)	1,3,5-Trinitrobenzene
1,2-Dichlorobenzene	4-methylphenol (p-Cresol)	**Surrogates:**
1,3-Dichlorobenzene	Naphthalene	2-Fluorobiphenyl
1,4-Dichlorobenzene	1,4-Naphthoquinone	2-Fluorophenol (320 mg/mL)
3,3-Dichlorobenzidine	1-Naphthylamine	Nitrobenzene-d5
2,4-Dichlorophenol	2-Naphthylamine	Phenol-d5 (320 mg/mL)
2,6-Dichlorophenol		p-Terphenyl-d14
		2,4,6-Tribromophenol (320 mg/mL)

- Life of Standard: 12-months or less as indicated by the manufacturers expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

5.5.1.2 Benzoic Acid- Initial Calibration Stock

The Benzoic Acid Stock is purchased from Cerilliant at a 1000 ug/mL concentration with 1 mL volume.

Benzoic Acid

- Life of Standard: 12-months or less as indicated by the manufacturer's expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

5.5.2 Calibration Standard – Parent (5 ug/L)

The Benzoic Acid Stock is purchased from Cerilliant at a 1000 ug/mL concentration with 1 mL volume. 15.625 uLs of the 8270 BNA Working Calibration Standard Stock (160 ug/L) is brought to a 500 uL volume with DCM, resulting in a concentration of 5 ug/L. This is stored in a 1.5-mL labeled amber, Teflon-top vial, at -10 to -20°C until needed. All preparation information is recorded in LabNet and assigned a LabNet ID Number. An expiration date is assigned for 6-months from date of preparation or less as indicated by the manufacturer.

5.6 Appendix IX Initial Calibration Stock Standards

The Appendix IX Supplemental Mix 2 Stock Standard, the EPA 8270/Appendix IX Semivolatile Stock Standard, the Aramite Stock Standard, the Hexachlorophene Stock Standard, and the p-Phenylenediamine Stock Standard are purchased from Supelco in 1.0 mL sealed amber-glass ampules. The standards are labeled with a LabNet ID Number and are stored at -10° to -20°C and can be kept for 1-year from the date of receipt or less as indicated by the manufacturer.

Each mixture contains the following compounds and concentrations:

8270 APIX Supplemental Mix 2 at 2,000 ug/mL	
Acetophenone	N-Nitrosodiethylamine
Isosafrole	N-Nitroso-di-n-butylamine
Pentachlorobenzene	N-Nitrosomethylethylamine
Phenacetin	2-Picoline
Methyl methanesulfonate	Safrole
N-Nitrosomorpholine	Hexachloropropene
N-Nitrosopiperidine	p-(Dimethylamino)azobenzene
N-Nitrosopyrrolidine	Ethyl methanesulfonate
Pentachloroethane	Pentachloronitrobenzene
o-Toluidine	3-Methylcholanthrene
1,2,4,5-Tetrachlorobenzene	1,3,5-Trinitrobenzene
1,3-Dinitrobenzene	1-Naphthylamine
2-Naphthylamine	2,3,4,6-Tetrachlorophenol
2,6-Dichlorophenol	2-Acetylaminofluorene
Dinoseb	4-Aminobiphenyl
4-Nitroquinoline-1-oxide	5-Nitro-o-toluidine
7,12-Dimethylbenz(a)anthracene	Diphenylamine

8270 Supplemental Mix 2 (Catalog #86141) at 2,000 ug/mL	
1,4-Dioxane	1,4-Naphthoquinone
1,4-Dinitrobenzene	1-Methylnaphthalene
a,a-Dimethylphenethylamine	Chlorobenzilate
Dibenzo(a,j)acridine	2,3,5,6-Tetrachlorophenol
Diallate	Isodrin
Kepone	Pronamide

Single Component Stock Standards	
Compound	**Concentration (ug/mL)**
Aramite	2,000
Hexachlorophene	5,000
p-Phenylenediamine	5,000

5.7 Initial Calibration Standards

Two separate initial calibrations are prepared; one for HSL and one for Appendix IX.

5.7.1 HSL Initial Calibration Standards –HP 5972 Instruments

5.7.1.1 8270 Benzidine Mix - Initial Calibration Stock

The 8270 Benzidine Mix Stock is purchased from Supelco at 2000 ug/mL concentration with 1 mL volume.

3,3'-Dimethylbenzidine
3,3'-Dichlorobenzidine
Benzidine

- Life of Standard: 12-months or less as indicated by the manufacturer's expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

NOTE: This solution is obtained from Supelco with a different lot number from the extraction spiking solution.

5.7.1.2 Surrogate Standard Solution - Initial Calibration Stock

The surrogate standard solution is obtained from Supelco (Catalog #861142) as a prepared solution in a 100 mL amber glass Teflon-lined screw-capped bottle. The surrogate standard is prepared by Supelco using EPA certified standards at the following concentrations:

Compound	Concentration (ug/mL)
p-Terphenyl-d_{14}	1000
Nitrobenzene-d_5	1000
2-Fluorobiphenyl	1000
Phenol-d_5	1000
2-Fluorophenol	1000
2,4,6-Tribromophenol	1000

- Life of Standard: 6-months from date of transfer of standard or less as indicated by the manufacturer's expiration date.
- Storage Requirements: Store at -10 to -20°C. All bottles are labeled with a LabNet ID Number.

5.7.1.3 HSL Initial Calibration Standards – HP 5972 Instruments

Remove the 8270 LCS Stock (see section 5.2.1), the 8270 Modified Surrogate Stock and the Benzidines Mix Stock standard as identified in Section 5.7 from storage. Allow the standards to come to room temperature. Transfer the stock standards to a 1.5-mL amber-glass, Teflon-lined, screw-capped vial. Record the transfer in LabNet and obtain a LabNet ID Number for each standard. Store the unused standard at -10° to -20°C.

Locate and rinse WELL with DCM, a 10 uL, 25 uL, 100 uL, 500 uL, and 1000 uL syringe.

The preparation information for the Working HSL Standards are entered into LabNet and each standard is given a LabNet ID Number. Prepare the Working Standards as follows:

Cal. Std.	BNA LCS Stock (200 ug/mL)	Surr. Stock (1000 ug/mL)	Benzidine Mix (2000 ug/mL)	DCM	Internal Std. (2000 ug/mL)
120 ng/uL	300 uL	60 uL	70 uL	Dilute to 0.5 mLs	*5 uL
100 ng/uL	250 uL	50 uL	62.5 uL	Dilute to 0.5 mLs	*5 uL
80 ng/uL	200 uL	40 uL	42.5 uL	Dilute to 0.5 mLs	*5uL
60 ng/uL	150 uL	30 uL	35 uL	Dilute to 0.5 mLs	*5 uL
50 ng/uL	125 uL	25 uL	31.25 uL	Dilute to 0.5 mLs	*5 uL
40 ng/uL	100 uL	20 uL	20 uL	Dilute to 0.5 mLs	*5 uL
20 ng/uL	50 uL	10 uL	10 uL	Dilute to 0.5 mLs	*5 uL
10 ng/uL	25 uL	5 uL	5 uL	Dilute to 0.5 mLs	*5 uL

* Add internal standard **after** the standard has been brought up to 0.5 mL.

The calibration levels listed above are correct for all compounds except Benzidine, 3,3'-Dichlorobenzidine and 3,3'-Dimethylbenzidine. The calibration levels for Benzidine, 3,3'-Dichlorobenzidine and 3,3'-Dimethylbenzidine are as follows:

Benzidine cal. levels	3,3'-Dichlorobenzidine	3,3'-Dimethylbenzidine
20 ng/uL	20 ng/uL	10 ng/uL
40 ng/uL	40 ng/uL	20 ng/uL
100 ng/uL	100 ng/uL	60 ng/uL
175 ng/uL	175 ng/uL	125 ng/uL
200 ng/uL	200 ng/uL	140 ng/uL
250 ng/uL	250 ng/uL	170 ng/uL
350 ng/uL	350 ng/uL	250 ng/uL
400 ng/uL	400 ng/uL	280 ng/uL

- Life of Standard: 6-months from date prepared or less as indicated by the manufacturer's expiration date.
- Storage Requirements: Store in an amber crimp-top autosampler vials at -10 to -20°C.

5.7.2 HSL Initial Calibration Standards – HP 5973 Instruments

Remove the 8270 BNA working standard and the Benzoic Acid Stock standard as identified in Section 5.5.1 from storage. Allow the standards to come to room temperature. Transfer the stock standards to 1.5-mL amber-glass, Teflon-lined, screw-capped vials. Record the transfer in LabNet and obtain a LabNet ID Number for each standard. Store the unused standard at -10° to -20°C.

Locate and rinse WELL with DCM, a 10 uL, 25 uL, 100 uL, 500 uL, and 1000 uL syringe.

The preparation information for the Working HSL Standards are entered into LabNet and each standard is given a LabNet ID Number. Prepare the Working Standards as follows:

Cal. Std.	BNA Working Std. (160 ug/mL)	Benzoic Acid (200 ug/mL)	DCM	Internal Std. (800 ug/mL)
80 ng/uL	250 uL	200 uL	Dilute to 0.5 mLs	*5uL
70 ng/uL	218.75 uL	175 uL	Dilute to 0.5 mLs	*5uL
50 ng/uL	156.25 uL	125 uL	Dilute to 0.5 mLs	*5 uL
40 ng/uL	125 uL	100 uL	Dilute to 0.5 mLs	*5 uL
20 ng/uL	62.5 uL	50 uL	Dilute to 0.5 mLs	*5 uL
10 ng/uL	31.25 uL	25 uL	Dilute to 0.5 mLs	*5 uL
5 ng/uL	15.625 uL	12.5 uL	Dilute to 0.5 mLs	*5 uL
2 ng/uL	200 uL of 5 ug/mL Parent Soln.	---	Dilute to 0.5 mLs	*5 uL
1 ng/uL	100 uL of 5 ug/mL Parent Soln.	---	Dilute to 0.5 mLs	*5 uL
0.5 ng/uL	50 uL of 5 ug/mL Parent Soln.	---	Dilute to 0.5 mLs	*5 uL
0.1 ng/uL	10 uL of 5 ug/mL Parent Soln.	---	Dilute to 0.5 mLs	*5 uL

* Add internal standard **after** the standard has been brought up to 0.5 mL.

- Life of Standard: 6-months from date prepared or less as indicated by the manufacturer's expiration date.
- Storage Requirements: Store in an amber crimp-top autosampler vials at -10 to -20°C.

5.7.2 Appendix IX Parent Solution - 200 ug/mL

Stock Standard	Concentration (ug/mL)	Amt. Added (uL)
8270 Calibration Mix 1	1,000	1000
8270 Supplemental Mix 2	2,000	500
Aramite	2,000	500
p-Phenylenediamene	5,000	200
Hexachlorophene	5,000	1600

The Appendix IX Parent Solution is brought up to a 3.0-mL final volume with DCM. The preparation is entered into LabNet and the standard is given a LabNet ID Number. An expiration date of 6-months is assigned or less as indicated by the manufacturer and the standard is stored in a 3.5-mL amber-glass, screw-capped vial with a Teflon septum at -10 to -20°C.

5.7.2.1 Appendix IX Parent Solution – (20 ug/mL)

50 uLs of the Appendix IX Parent Solution (200 ug/L) is brought to a 500 uL volume with DCM, resulting in a concentration of 20 ng/uL. This is stored in a 1.5-mL labeled amber, Teflon-top vial, at -10 to -20°C until needed. All preparation information is recorded in LabNet and assigned a LabNet ID Number. An expiration date is assigned for 6-months from date of preparation or less as indicated by the manufacturer.

5.7.3 Appendix IX Initial Calibration Standards

Remove the Appendix IX stock standards as identified in Section 5.6 from storage. Allow the standards to come to room temperature. Transfer the Appendix IX stock standards to 1.5 mL amber-glass, Teflon-lined, screw-capped vials. Enter the transfer information into LabNet and obtain ID Numbers for each standard. Store the Appendix IX stock standards at -10°C to -20°C.

Locate and rinse WELL with DCM, a 10 uL, 25 uL, 100 uL, 500 uL, and 1000 uL syringe.

The preparation information for the Working Initial Calibration Appendix IX Standards is entered into LabNet and each standard is given a LabNet ID Number. Prepare the Working Standards as follows:

Calibration Std.	App. IX Parent Std. (200 ug/mL)	DCM	Internal Std. (2,000 ug/mL) (800 ug/mL for HP 5973's)
80 ng/uL	200 uL	Dilute to 0.5 mLs	*5 uL
60 ng/uL	150 uL	Dilute to 0.5 mLs	*5 uL
50 ng/uL	125 uL	Dilute to 0.5 mLs	*5 uL
40 ng/uL	100 uL	Dilute to 0.5 mLs	*5 uL
20 ng/uL	50 uL	Dilute to 0.5 mLs	*5 uL
10 ng/uL	25 uL	Dilute to 0.5 mLs	*5 uL
5 ng/uL	12.5 uL	Dilute to 0.5 mLs	*5 uL

*Internal Standard added after each standard is brought to a 0.5 mL final volume with DCM.

The calibration levels listed above are correct for all compounds except the following for Hexachlorophene:

640
560
400
320
160
80
40

- Life of Standard: 6-months from date prepared or less as indicated by the manufacturers expiration date.
- Storage Requirements: Store in amber crimp-top autosampler vials at -10 to -20°C.

5.8 Calibration Verification Standards

5.8.1 HSL Calibration Verification Standard

Remove the BNA working standard (160 ug/mL), the DFTPP/DDT (1000 ug/mL) Stock Standard, and the Benzoic Acid stock (200 ug/mL) standard from storage. Allow the standards to come to room temperature. Alternately, a calibration verification standard is analyzed once per year at a different concentration from our normal 40 ug/mL per NELAC. This is achieved by running a calibration verification at 50 ug/mL.

Locate and rinse WELL with DCM, a 10 uL, 25 uL, 100 uL, 500 uL, and 1000 uL syringe.

The preparation information for the HSL calibration verification check standard is entered into LabNet and each standard is given a LabNet ID Number. Prepare the HSL calibration verification check standard weekly as follows:

Cal. Std.	BNA Working STD. (160 ug/mL)	Working DFTPP/DDT Mix (optional) (1000ug/mL)	Benzoic Acid (200 ug/mL)	DCM	Internal Std. (2,000 ug/mL) (800 ug/mL for HP 5973's)
40 ng/uL	125 uL	25uL	100 uL	Bring to 0.5 mL	*5 uL
50 ng/uL	156.25 uL	25 uL	125 uL	Bring to 0.5 mL	*5 uL

* Add internal standard **after** the standard has been brought up to 1.0 mL.

- Life of Standard: 1-week from date prepared or less as indicated by the manufacturer's expiration date.
- Storage Requirements: Store in an amber crimp-top autosampler vials at -10 to -20°C.

5.8.2 Appendix IX Calibration Verification Standard

The Appendix IX calibration verification standard is prepared from the stock standards listed in Section 5.5.2. Bring the stock standards from storage and allow them to come to room temperature.

Locate and rinse WELL with DCM, a 10 uL, 25 uL, 100 uL, 500 uL, and 1000 uL syringe. The preparation information for the Appendix IX calibration verification check standard is entered into LabNet and the standard is given a LabNet ID Number. Prepare the Appendix IX calibration verification check standard as follows:

Calibration Std.	Appendix IX Parent Std. (200 ug/mL)	DCM	Internal Std. (2,000 ug/mL) (800 ug/mL for HP 5973's)
50 ng/uL	125 uL	Brought to 0.5 mL	*5 uL

* Internal Standard is added after the standard is brought up to 0.5 mL.

The calibration level listed above are correct for all compounds except for the following:

Compound	Calibration Std.
Hexachlorophene	320 ng /uL

- Life of Standard: 6-months from date prepared or less as indicated by the manufacturer's expiration date.
- Storage Requirements: Store in an amber crimp-top autosampler vials at -10 to -20°C.

6.0 CALIBRATION

Before any instrument is used as a measuring device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument. Preparation of all reference materials used for calibration is documented.

6.1 Initial Calibration

An initial calibration is completed:

- as needed - calibration verification cannot be met;
- after a source cleaning and/or column change; and
- anytime a major repair or change has occurred with the instrument that affects calibration.

Confirm that the GC/MSD is stable and equilibrated. If possible, allow the instrument to equilibrate overnight at all operating temperatures if the source/column has been cleaned/ changed.

Prior to beginning initial calibration:

- check the interface nut for security;
- check the vacuum (at 40°C - its normally between 4 and 5 x 10^{-5} torr);
- check the background, air/water levels and base ion by scanning for appropriate ions (44,32,28,18) and visually inspecting the spectrum scan [base ion is normally 28 (nitrogen) and good background levels are below 2000]; and
- check the stability of inlet helium flow generated by the Electronic Pressure Control (EPC).

A hard copy of the ion scans and background scan is set aside to be placed with the final autotune report and profile scan.

6.2 PFTBA Autotune or Manual Tune

The instrument is first tuned in one of two ways: autotune or manual tune. The ion abundances in the calibration gas (Perfluorotributylamine-PFTBA) are monitored at a temperature of 40°C and a column flow of 1.0 mL/minute. Monitoring at this temperature and flow produces the most representative cal gas scan, and therefore the best estimate of DFTPP response.

6.2.1 Set oven temperature to 40°C.

6.2.2 If an AUTOTUNE is to be performed, continue below. If not, continue to Section 6.2.5. An autotune is generally performed when the instrument has been down for maintenance (i.e., source cleaning or other non-routine maintenance).

6.2.3 After running an autotune, note the following:

6.2.3.1 Observe peak shape, absence of fronting, tailing, and the resolution between isotopes and mass axis for 69, 219 and 502 in the profile scan. The following is a guideline for the ratios of 69, 219, and 502, which indicate the source is operating properly.

Autotune report	
Isotope	**% of 69**
69	100 %
219	> 40 %
502	> 1 %

6.2.3.2 If the %'s do not meet these limits, the DFTPP standard will most likely not meet the required criteria. In addition, this is probably an indication that the source is not operating properly or perhaps the source is assembled incorrectly or it is dirty. Repeat the Autotune process and re-evaluate. If it still does not meet these limits, refer to the MSD manual for troubleshooting suggestions.

6.2.4 If the AUTOTUNE results are consistent with the limits above, go into MANUAL TUNE and save the AUTOTUNE values into the DFTPP tune file. The DFTPP tune file is used by the methods in setting the tune values (i.e. entrance lens, ion focus, etc..) to the values that were set in MANUAL TUNE. Once in MANUAL TUNE, adjust the tune parameters to meet the following limits:

Manual Tune Report	
Isotope	**% of 69**
69	100%
219	30-50%
502	1-2.5%

If unable to achieve these %'s redo an AUTOTUNE, and if still unsuccessful, refer to the MSD manual for troubleshooting suggestions.

6.2.5 If an AUTOTUNE has NOT just been performed, perform a MANUAL TUNE and adjust any parameters, if need be, to meet the relative abundances listed above. Adjustment may not be necessary, and not desired, if no previous problems have been encountered in meeting tune and calibration verification criteria. Hardcopy the profile scan and store the tune in the appropriate tune file.

6.3 DFTPP Analysis

Once the instrument is tuned, a 50 ng/uL injection of DFTPP must meet certain criteria. 1uL of the working DFTPP/DDT/PCP/Benzidine standard, containing 50 ng/uL of DFTPP/DDT/PCP and 100 ng/uL of Benzidine is analyzed by the method in Attachment 1. Alternately, DFTPP can be added to the calibration verification solution and run at the same time as the calibration verification run. The method outlined in Attachment 1 is an example and minor adjustments often have to be made to the method in regards to scan start/ending time.

The manner of acquiring the mass spectrum of DFTPP can be performed in only two specific ways with Target software:

- Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is performed and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. This procedure of averaging and subtracting is performed automatically by the Target software and evaluated by the criteria in Table 4. If this procedure does not meet the acceptance criteria in Table 4, then the analyst will use the following procedure:

- One scan of the DFTPP peak is acquired and not subtracted and evaluated by Target software using the criteria in Table 4. This procedure is performed manually by the analyst. No other manner of DFTPP acquisition and evaluation can be utilized.

The abundance's of designated masses MUST meet the criteria in Table 4, prior to any further analysis. In the acceptance criteria for DFTPP, certain ions have ratio acceptance criteria that are exclusive of the upper or lower limits of their acceptance range (i.e., ion m/z 70 must be less than 2.0 % of ion m/z 69). If in the event that a ratio on the DFTPP report generated by the Target software system lists the ratio of an ion at the limit of its acceptance range (i.e., ion m/z 70 is reported at 2.0%) and the ion is not flagged as being unacceptable, then the analyst will manually calculate the ion's ratio and confirm that the ion meets the ratio acceptance criteria as specified in Table 4.

6.4 Analysis of Initial Calibration Standards

The HSL initial calibration and the Appendix IX initial calibration are usually analyzed on separate 12-hour tunes. Each calibration standard is analyzed according to the method in Attachment 3. The method outlined in Attachment 3 is an example and minor adjustments often have to be made to the method in regards to scan start/ending time. The electron multiplier (EM) voltage should remain constant corresponding to the voltage of the DFTPP analysis. Characteristic ions and approximate retention times of the target compound are listed in Table 2.

6.4.1 Analyze an initial calibration.

6.4.1.1 Quantitate each standard and update the calibration into the appropriate method.

6.4.1.2 Print an instrument generated Initial Calibration (Attachment 4). Review the initial calibration and confirm that all compounds are integrated correctly and that all Calibration Check Compounds (CCC) and System Performance Check Compounds (SPCC) are within control limits. (Refer to Table 5 for a listing of the SPCC and CCC compounds.) All CCC's must have %RSD (Relative Standard Deviation) <15%, and all SPCC's must have an average minimum response factor (RF) greater than 0.05. Any CCC compound with a % RSD > 15% can be used if it meets the minimum coefficient of determination in a regression curve. Section 6.4.1.3 states the process for minimum acceptability for a CCC compound. The data system calculates all RF's and %RSD and the calculation is as follows:

$$RF = \frac{A_t}{A_i} \times \frac{C_i}{C_t}$$

Where:
A_t= Area of target compound
A_c= Area of internal standard
C_i = Concentration of internal standard
C_t = Concentration of target compound

6.4.1.3 Application of Regression Curves in the Initial Calibrations (8270C)

For all compounds in the initial calibration with a %RSD >15.0%, calibration curves of area ratio versus concentration using a first or higher order regression curve of the calibration curve points will be performed. A first order linear regression or weighted linear regression will be used if it gives the highest correlation coefficient and if the y-intercept is > 0. Otherwise, a second or third order regression curve will be used.

Method 8000B/8270C specifies a minimum coefficient of determination of 0.990 (R^2=0.9801). The methods also specify a minimum of 5 calibration points for a linear (first order) model and a quadratic (second order) model requires six points. The laboratory, in order to meet AFCEE requirements, will analyze a minimum number of points to satisfy both SW-846 and AFCEE. For further reference of how initial calibration curves are evaluated refer to in "GC/MS Calibration - Evaluation and Acceptance Criteria" (Attachment 6).

The recipes noted above will be modified to include the necessary calibration levels. Recipes are for guidance only and may change as needed.

Note: South Carolina does not allow the use of quadratic curves for initial calibrations. If the %RSD criteria are not met, only the linear regression model will be used. This will be considered a project-state-specific requirement.

6.4.2 Having met the required criteria listed in Attachment 6, initial calibration is acceptable and complete. An example of an acceptable initial calibration appears in Attachment 5. If samples are analyzed on the same 12-hour tune as the initial calibration, the calibration standard in the initial calibration corresponding to the calibration verification standard must pass the requirements of the daily calibration as listed in Section 6.5. The samples will be quantitated using the response factors from the initial calibration for Method 8270C.

6.4.3 Initial calibrations are generally performed on an "as needed basis" (i.e., continuing calibration standard cannot be met) or after major maintenance (i.e., source cleaning, column change) have been performed.

6.4.4 Refer to the STL Corporate Procedure, P-T-001, 'Selection of Calibration Points' (Attachment 2) or on STLs Intranet.

6.4.5 Several programs require the analysis of a second-source standard, following the initial calibration and prior to the analysis of samples. The recovery limits for the SSV (IcalSpike) spike can vary from project to project. Corrective actions for out-of-control compounds in the SSV are assessed on a case-by case basis.

6.5 Calibration Verification

A calibration verification occurs every 12 hours of run-time. All DFTPP requirements must be met. After having satisfied these requirements, a daily calibration verification must be met.

6.5.1 Analyze 1 uL of the HSL calibration verification check standard according to the method specified in Attachment 3. If the Appendix IX compounds specified in Section 5.5.2 are to be analyzed, then the Appendix IX calibration verification standard will also be analyzed on the same 12-hour tune according to the method specified in Attachment 3. The method outlined in Attachment 3 is an example and minor adjustments often have to be made to the method in regards to scan start/ending time. The electron multiplier (EM) voltage should remain constant according to the voltage of the DFTPP analysis.

6.5.1.1 Confirm that the average response for all analytes is within 15% (grand mean). This verifies that the calibration verification meets Method 8000B criteria. If the verification meets 8000B criteria then proceed to check for additional criteria as stated in Method 8270C in Section 6.5.1.2. If the calibration verification does NOT meet 15% (grand mean), then check the operating conditions, and if necessary perform minor instrument maintenance (Sec. 7.5.1). Inject another calibration verification standard. If the

response for the analytes is still not within 15%, then a new initial calibration must be analyzed.

6.5.1.2 Confirm that all compounds are integrated correctly and that all CCC's and SPCC's have met the required criteria. For Method 8270C, all RSD's for the CCC's must have a percent difference (%D) < 20% in relation to the initial calibration or <20% drift for measured concentrations of CCC compounds that had a first or higher order initial calibration regression curve. All SPCC's must have a minimum RF greater than 0.05.

$$\% \text{ Drift} = \frac{C_i - C_c}{C_i} \times 100$$

Where:
C_i = CCC standard concentration (50 ng)
C_c = measured CCC concentration

6.5.1.3 All internal standard retention times must not have changed more than 30 seconds from the last calibration verification standard. All internal standard areas must not change by a factor of 2 (-50% to +100%) from the midpoint standard in the HSL initial calibration.

6.5.1.4 For Method 8270C, all quantitation is performed using the initial calibration.

6.5.2 If both the DFTPP and calibration verification standard have met the required criteria, analysis can proceed.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Control is accomplished through 1) daily tuning and calibration checks and 2) preparation QC traceable through individual extraction batches.

NOTE: Table 1 contains the laboratory internally-derived statistical control limits for the MS/MSDs, the LCS, and the surrogates. The limits used to assess precision and accuracy as well as the number of compounds being used for bench level control may vary with client, QAP, project, etc.. This information is transmitted to the bench via the COC, kick-off meetings, tech profiles, etc..

7.1.1 Initial Calibration

PFTBA
DFTPP.....Prior to initial calibration
Initial Cal. Stds.....Prior to samples
SSV (IcalSpike).....Prior to samples

7.1.2 Daily Analysis

PFTBA
DFTPP.....Prior to calibration verification
Daily Cal. Stds.....Prior to samples
Samples *

*Any given 12-hour period may contain various quality controls. Preparation QC is at a 5% frequency. Instrumental controls are outlined above and further discussed in the procedure section.

Prep QC	Frequency
MB	1 per batch [3]
LCS [1]	1 per batch
MS/MSD's [2]	1 set in batch
Surrogates	Every sample / MB / LCS / MS / MSD

[1] LCS Duplicate (LCD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract....pre-determined by the extraction department.
[2] The sample selection for MS/MSD are rotated among client samples so that various matrix problems may be noted and/or addressed. ....pre-determined by the extraction department.
[3] A batch is not to exceed 20 samples.....pre-determined by the extraction department.

Every attempt is made to run a full extraction batch or at the minimum its associated blank, within the same 12-hour period or next 12-hour period, on the same instrument, to keep the preparation QC as reflective of the entire analysis as possible. If, for TAT reasons, a portion of the batch must be analyzed quickly and far in advance of the rest of the batch, the MB may be re-analyzed with the remainder of the batch. The MS/MSD is analyzed once, with their respective client.

7.2 Sample Preservation and Storage

Sample containers, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance and/or specific contract or client requests (Refer to the BNA Extraction SOPs for Methods 3510C, 3520C, 3550B, 3541 and 3580A for more specific information). Listed below are the holding times and the references that include container and preservation requirements for compliance with SW-846. Holding times prior to extraction are:

Matrix	SW-846 (VTS)[1]	Preservation
Soil/Sediment	14 days	Cool 4 ± 2°C
Water	7 days	Cool 4 ± 2°C
Waste / Oil	14 days	Cool 4 ± 2°C

[1]VTS = verified time of sampling

All samples extracted for BNA analysis are stored in extraction batches, in 1.5 - 2.0 mL screw-capped Teflon-lined vials or appropriately sized ground-glass volumetric, at 4 ± 2°C in the dark until analysis. All extracts are analyzed within 40 days of extraction.

7.3 Sample Preparation

7.3.1 Waters - Samples Extracted by Methods 3510C / 3520C

Samples (waters, aqueous sludges) prepared by Methods 3510C/3520C, produce ~1-mL extracts containing both the acid and base/neutral fractions. Dilute the extract up to the final 1-mL volume with DCM.

Samples that are suspected to have high levels of organic contamination are screened prior to analysis. Based on the screener result, an initial dilution may be performed.

500 uLs extract + 5 uLs Internal Standard.

This leaves 500-uLs extract remaining for secondary dilutions or a repreparation.

7.3.2 Soils, Sediments, Organic Sludges Extracted by SW 3541 / 3550B / 3580A

These samples prepared by one of the above reference methods; results in one 1-mL extract (0.5 mL extract volume for 3541). Dilute the extract up to the final volume with DCM.

Samples that are suspected to have high levels of organic contamination are screened prior to analysis. Based on the screener result, an initial dilution may be performed.

500 uLs extract + 5 uL Internal Standard for 3550B or 3580A.
250 uLs extract + 2.5 uL Internal Standard for 3541.

This leaves ½ volume of the extract remaining for secondary dilutions or a repreparation. Normal waste samples have a final volume of 10 mLs and are prepared as defined above.

7.4 Calibration Standardization

Refer to Section 6.0. Instrument calibration is based on a 12-hour tune or the calibration is completed on an as-needed basis (Section 6.1).

7.5 Preventive Maintenance

Instrumental maintenance can be broken down into three categories: daily, yearly, and "as required".

7.5.1 Daily Maintenance

- Change injection port septum.
- Check and replace liner.
- Remove column nut, check graphite ferrule - replace if necessary, and trim column.
- Check detector nut and be sure it is tightened completely.
- Replace rinse DCM
- Bake out the GC at 300°C for ~30 minutes

7.5.2 Yearly Maintenance

The only scheduled yearly maintenance involves the changing of the roughpump oil.

7.5.3 "As Required" Maintenance

Most maintenance is performed on an "as needed" basis, is operator determined and can be categorized as GC or MSD related.

Each required maintenance may be performed for a variety of reasons. Certain trouble-flags will indicate what maintenance procedures may be required. Refer to the GC/MSD Maintenance Manual for procedures, references, and documentation of maintenance actions. All maintenance or significant occurrences are entered into the instrument maintenance logbook with a reference number. This reference number is also written into the appropriate operator's logbook on the date in question.

7.5.3.1 GC related

- Clean injection port, swab out inlet with Methanol.
- Sonicate/clean or replace gold seal, washer, and reducing nut.
- Change column. Use DB5MS, 30m-x 0.25 mm ID x 0.25um, bonded-phase silicone coated fused-silica capillary column. Condition the column as follows:

Set oven program to:	initial temp = 40°	initial time = 30 min.
Rate= 1°/min	final temp = 300°	final time = 60 min.

NOTE: Be sure there is flow through the column.

- Check Helium flow rate to inlet and the stability of the Electronic Pressure Control (EPC); clean or replace injection port lines.
- Change gas cylinder once 500 psi is attained, change oxy-trap every other cylinder, check for leaks.
- Clean liners and store in sylon.

7.5.3.2 MS Related

- Check vacuum, and interface nut;
- Clean source and anything associated with that activity. Refer to the MSD maintenance manual for details concerning source disassembly, cleaning, and reassembly.

7.6 Sample Analysis

7.6.1 Analyze 1 uL of sample by the method listed in Attachment 3. The method outlined in Attachment 3 is an example and minor adjustments often have to be made to the method in regards to scan start/ending time. The analysis method should remain constant corresponding to the conditions of the calibration verification standard(s).

7.6.2 After quantitation, any extract showing analytes of interest exceeding the calibration range is appropriately diluted and re-analyzed.

7.6.3 Extracts are stored after analysis at $4\pm2^{\circ}C$ until disposal. Extracts are kept for a period of 1 year from the date of analysis.

7.7 Documentation

7.7.1 Sample Analysis and Tracking

The preparation and analysis is recorded in the GC/MS Semi-Volatile Analysis Logbook, and must be completed for each days analysis (Attachment 7).

7.7.2 Data Management

Although there is a substantial amount of space available to both BNA's and VOA's during busy periods, the system can fill rather quickly. As an estimate, a maximum of about 3 months (per instrument) can be kept on the system at one time. There is not necessarily a set definite schedule of removing data from the system. No data is removed from the system until it has been archived on at least one full back up and a number of differential back-ups.

7.7.3 Archival of Data

Back-ups are scheduled to occur automatically through the ARCServe software. There are four types of back-ups that are performed on the Server.

- A differential back up is performed Monday through Thursday. These occur at 1:00AM each day. The differential tape must be in place by this time and is loaded the night before (usually). These tapes are over-written each week. Differential tapes are located at the server.
- The Server automatically back-up the archive database information, regardless of the tape that is in the drive. This is performed in the unlikely event that ARCServe crashes and the database (the archive-logs) is deleted. Duration of this event is ~3 minutes and takes place immediately after the differential and full back-ups.
- Every Tuesday a full-system back up is performed. A blank archive tape is required for each Friday back up. Depending on the amount of data, more than one tape may be necessary. Full tapes are never over-written. The most current full tapes are stored down in the office area. Older tapes are in locked storage.
- Every Wednesday a system back up is performed. There are four tapes provided for this back up, and are rotated each week.

The system maintains a database, or logs, of each back-up session. Successful completion of each back up can be verified each morning by accessing the job report logs in ARCServe. This is performed each morning. Any missed jobs can be re-scheduled and completed in the morning of the following day. As noted above, this database is re-archived after every normal back-up and can be retrieved at anytime necessary.

8.0 QUALITY CONTROL

8.1 QC Summary

The department will review the quality controls as follows:

8.1.1 At least one MB will be included in each extraction set (maximum of 20 samples). The MBs will be examined to determine if contamination is being introduced in the laboratory. The corrective action policy for MBs is found in Section 8.2.10.

8.1.2 One LCS will be included in each extraction set (maximum of 20 samples). Two LCS samples will be extracted when insufficient sample is available for the MS/MSD. When two LCS's are performed, they will be examined to determine both precision and accuracy. The corrective action policy for LCS samples is found in Section 8.2.11.

Accuracy will be measured by the percent recovery (%R) of the LCSs. The recovery must be in range, as determined by statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

8.1.3 Surrogate compounds will be added to every sample to measure performance of the analysis. Results must agree within statistical control limits in order to be considered acceptable.

8.2 Corrective Action

There are two corrective action reports in use in the GC/MS BNA analysis: the CAR/Qualifications Report Logbook and the Sample Corrective Action Report.

8.2.1 The GC/MS BNA CAR/Qualifications Report

This logbook is specific for each GC/MS BNA instrument and is used to provide corrective action for the analysis of DFTPP, Initial Calibrations, Calibration Verifications, Internal Standard Areas (continuing calibration standard to continuing calibration standard) and Qualification of Data (Attachment 7). The description of the situation, the corrective actions taken, the demonstration of control, and any data qualification are documented. The corrective action report is initiated using the Tune File Number as a reference. This provides a tracking mechanism through the entire analytical process, therefore allowing for the qualification of data in the case narrative.

8.2.2 DFTPP

If in the event that upon analysis of DFTPP at 50 ng/uL the ion ratios do not meet the acceptance criteria listed in Table 4, the analysts must perform the following:

8.2.2.1 The description of the situation is documented in the GC/MS BNA Corrective Action (CAR)/Qualification Report Logbook, thus initiating the corrective action process.

8.2.2.2 All corrective actions taken must be documented in the CAR/Qualifications Report and may include some but not all of the following:

- confirm that the DFTPP standard solution has not degraded or has not expired;
- inspect the GC and/or MS system for malfunction or problem that may suggest the need for instrument maintenance as listed in Section 7.5; and
- retune using PFTBA and reanalyze the DFTPP at 50 ng/uL.

8.2.2.3 Upon reanalysis of DFTPP that meets the acceptance criteria listed in Table 4, the demonstration of control must be documented in the CAR/Qualifications Report Logbook. It is the policy of the BNA lab that: **No further analysis will be performed using this method until an acceptable DFTPP analysis has been successfully performed.**

8.2.3 Initial Calibration

8.2.3.1 If in the event the initial calibration does not pass acceptance criteria as specified in Section 6.4.1.2 and in Attachment 6, the analyst must perform the following:

- The description of the situation is documented in the GC/MS BNA Corrective Action (CAR)/Qualification Report Logbook, thus initiating the corrective action process.

- All corrective actions taken must be documented in the CAR/Qualifications Report and may include some but not all of the following:

  - confirm that the initial calibration standard solutions have not degraded or have not expired; prepare new standards if suspect; reanalyze DFTPP and the initial calibration;
  - inspect the GC and/or MS system for malfunction or problem that may suggest the need for instrument maintenance as listed in Section 7.0; perform any necessary maintenance or correct instrument problem; rerun DFTPP and initial calibration; and
  - inspect data and rerun any or all of the initial calibration curve points.

Upon performance of an initial calibration that meets the acceptance criteria listed in Section 6.4.1.2 and the table in Attachment 6, the demonstration of control must be documented in the CAR/Qualifications Report Logbook.

If in the event that samples must be analyzed using an out-of-control initial calibration due to analysis hold time considerations or a client specified acceptance of this initial

calibration due to a rush TAT, the qualification of data effected must be documented in the CAR/Qualifications Report Logbook and addressed in the case narrative.

8.2.4 Calibration Verification

If in the event the calibration verification does not pass acceptance criteria as specified in Section 6.5.1, the analyst must perform the following:

8.2.4.1 The description of the situation is documented in the GC/MS BNA Corrective Action (CAR)/Qualification Report Logbook, thus initiating the corrective action process.

8.2.4.2 All corrective actions taken must be documented in the CAR/Qualifications Report and may include some but not all of the following:

- When a CCV exceeds it's recommended acceptance criteria, inspect the system to determine the cause and restore original conditions. Reanalyze the standard or prepare a new standard. Document all actions / reasons in the comment section of each runlog. **Under no circumstances is a CCV to be re-injected prior to completing the aforementioned reviews; or automatically injecting 2 CCV's.**
- There are various types of instrument maintenance that should not automatically require recalibration. Examples include changing/adjusting: septa; compressed gas cylinders; syringes; moisture, hydrocarbon or oxygen traps; split seals; column fittings; inlets; or filaments. Other procedures include breaking off or changing a guard column or cleaning the inlet. Whenever such procedures are performed, the analyst must demonstrate that the results for a CCV meet the prescribed acceptance limits before analysis of any samples. Otherwise, recalibration is required.
- If the % recovery(s) are still out-of-control, a new calibration sequence (linearity) is required, and all samples that were injected after the last in control standard must be reanalyzed.
- Maintenance procedures that automatically require recalibration include: changing the column; changing the entrance lens, draw out lines or repeller; cleaning the MS source; changing the electron multiplier, ion source chamber or injector port. Whenever such procedures are performed, the analyst must perform a new ICAL that meets the method requirements. Changing or replacing the column will also require that the retention time windows will need to be re-determined.

8.2.4.3 Upon reanalysis of the calibration verification that meets the acceptance criteria listed in Section 6.5.1, the demonstration of control must be documented in the CAR/Qualifications Report Logbook.

8.2.4.4 If in the event that samples are analyzed using an out-of-control calibration verification due to analysis hold time considerations or a client specified acceptance of

this calibration verification, the qualification of data effected must be documented in the CAR/Qualifications Report Logbook and addressed in the case narrative.

8.2.5 Internal Standard Areas/Retention Times

If in the event the internal standard areas or retention times of the calibration verification do not pass acceptance criteria as specified in Section 6.5.1, the analyst must perform the following:

8.2.5.1 The description of the situation is documented in the GC/MS BNA Corrective Action (CAR)/Qualification Report Logbook, thus initiating the corrective action process.

8.2.5.2 All corrective actions taken must be documented in the CAR/Qualifications Report and may include some but not all of the following:

- confirm that the calibration verification standard solutions have not degraded or has not expired; prepare new standards if suspect; reanalyze DFTPP and the calibration verification.
- inspect the GC and/or MS system for malfunction or problem that may suggest the need for instrument maintenance as listed in Section 7.0; perform any necessary maintenance or correct instrument problem; retune PFTBA, rerun DFTPP and reanalyze the calibration verification.

8.2.5.3 Upon performance of a calibration verification that meets the acceptance criteria listed in Section 6.5.1, the demonstration of control must be documented in the CAR/Qualifications Report Logbook.

8.2.5.4 If in the event that samples are analyzed using an out-of-control calibration verification standard due to analysis hold time considerations or a client specified acceptance of this calibration verification, the qualification of data effected must be documented in the CAR/Qualifications Report Logbook and addressed in the case narrative.

8.2.6 The Sample Corrective Action Report

The Sample Corrective Action Report (CAR) (Attachment 8), is attached to the back of every chain-of-custody and is used to provide corrective action for the analysis of samples, MS/MSDs, MBs, and LCSs. The Sample CAR is a tracking system for the decision making process in regards to corrective action for dilutions, internal standards, surrogate recoveries or any other occurrence that is identified in the aforementioned analyses. The corrective action for a set of samples is tracked using the DFTPP tune file on the Sample CAR. The decision for a corrective action on a sample are initialed and dated by the analyst. All sample analyses are tracked on this form even if there is not a corrective action required.

Out-of-control situations are identified upon initial data review/reduction immediately following sample analysis. The analyst must perform the following steps before an out-of-control situation is identified. The analyst should:

- rule out any instrument malfunction or mis-injection of the sample;
- verify that all peaks of interest are integrated completely;
- verify that all calculations are correct;
- verify concentrations of surrogates/spikes in the spiking solutions are correct;
- verify that the sample was prepared correctly and that the correct amount of ISTD was added;
- verify that the ISTD and surrogate areas are reasonable; and
- verify that if a dilution was made was it prepared correctly

8.2.7 Dilution Corrective Action Policy

Upon the identification of an out-of-control event concerning a sample needing either an alternate initial dilution or a secondary dilution, the corrective action decision is documented on the Sample CAR. The analysis of the dilution is also recorded on the Sample CAR, indicating that the dilution was successful, thus demonstrating a return to control, or that additional dilutions may be required.

An alternate initial dilution may be required if in the opinion of the analyst that in the first analysis the sample background matrix has saturated the detector. The sample would require a reanalysis at a dilution and is considered the initial analysis. The necessary initial dilution level is documented on the Sample CAR with the initials of the analysts and the date.

A secondary dilution on a sample must be performed if the on-column quantitation of any target compound exceeds the linear range of the initial calibration curve (80-ng on-column). The necessary secondary dilution level is documented on the Sample CAR with the initials of the analyst and the date the sample on the report.

8.2.8 Screening of Samples

All samples suspected of being high in target and non-target compounds are screened on a GC/MS instrument. Initial sample dilutions are determined from this screening analysis. All efforts are made to run all samples undiluted to achieve the lowest reporting limits possible. However, severe matrix effects will result in the laboratory running initial dilutions to obtain the best chromatography possible and reduce damage to our instrumentation and columns. Severe matrix effects can be defined as any unknown peak which is at least two times the peak height of its applicable internal standard or any group of peaks that results in peak heights one time above their respective internal standard. The laboratory will use professional judgment in determining initial dilutions. The laboratory will make all attempts to obtain surrogate recoveries in all initial dilutions but generally they are not achievable in dilutions of fifty times or greater (5973 instruments) or ten times or greater (5972 instruments).

8.2.9 Internal Standard Areas / Retention Times Corrective Action Policy

The internal standard areas in any sample analysis will not vary by more than a factor of two (-50% to +100%) from the internal standard areas in the corresponding calibration verifications standard. Most AFCEE/LCG clients require (-50% to +100%) from the internal standard retention times in the corresponding initial calibration mid-point calibration standard. The internal standards in the samples will not vary in retention time by more than ±30 seconds from the internal standard retention times in the corresponding calibration verifications standard (most AFCEE/LCG clients require ± 30 seconds from the internal standard retention times in the corresponding initial calibration mid-point calibration standard). Upon the identification of an out-of-control event in a sample analysis (in regards to internal standard areas or retention times), the corrective action is documented on the Sample CAR with the decision whether to reanalyze the sample, initialed and dated.

8.2.9.1 The decision to reanalyze a sample is based on the following criteria:

- All samples, MS/MSD's, MB, and LCS samples will be reanalyzed due to a shift in the retention time of the internal standards.
- A secondary dilution is considered a reanalysis for a sample with internal standard areas outside of the acceptance limits. A reanalysis is not required on a secondary dilution with internal standard areas outside of acceptance limits.
- Reanalysis of MS/MSDs and LCS samples are not performed due to internal standard areas.
- If the sample and the MS/MSD on that sample exhibit similar internal standard area patterns, then the sample does not require a reanalysis.
- Samples with out-of-control internal standard areas do not require a reanalysis if in the opinion of the analyst and with the approval of the supervisor or section manager the following situation(s) occur:
  - there is obvious matrix interference in the samples causing the internal standard areas to be out-of-control.
  - there are no target compounds detected in the sample greater than the reporting limit that uses the out-of-control internal standard for quantitation.
  - there is approval given by supervisor, the section manager, the Project Manager, or the client that a reanalysis is unnecessary.

8.2.9.2 The results of a sample reanalysis due to out-of-control internal standards are documented on the Sample CAR.

If upon reanalysis of the sample, the internal standards meet the acceptance criteria, the documentation of return to control is recorded on the Sample CAR, and the reanalysis is reported as the initial analysis.
If upon reanalysis of the samples the internal standard is still out-of-control, this is documented in the Sample CAR. Both the initial and reanalysis is reported on the sample. All corrective action decisions are addressed in the case narrative.

8.2.10 Surrogate Recovery Corrective Action Policy

The surrogate recovery QC limits for both water and soil matrices are found in Table 1. Upon identification of an out-of-control event in regards to surrogate recoveries, the corrective action will be documented in the Sample CAR and the decision of whether to re-extract the sample is initialed and dated by the analyst. The sample re-analysis or re-extraction/reanalysis is also documented on the Sample CAR. This provides a documentation of a return to control or situation that requires addressing in the case narrative.

8.2.10.1 The decisions regarding corrective action for out-of-control surrogate recoveries are made using the following policies:

- If any surrogates are outside of limits in the MB, the MB may be reanalyzed. If the surrogate recoveries are also out-of-control in the reanalysis, the entire extraction batch will have to be re-extracted and reanalyzed.
- LCS samples do not require re-extraction due to out-of-control surrogate recoveries nor do associated samples require re-extraction.
- MS/MSD samples do not require re-extraction due to out-of-control surrogate recoveries.
- If one surrogate in any one sample is out of limits and all surrogate recoveries are greater than 10%, then the sample does not require re-extraction. If one acid and one base-neutral is out of limits in any one sample analysis and all surrogate recoveries are greater than 10%, then the sample does not require re-extraction.
- If the sample with the out-of-control surrogates is the same sample on which the MS/MSD was performed, and the MS/MSD show the same recovery pattern, then a re-extraction on the sample is not required.

A re-analysis of the sample is suggested before continuing. If an entire batch is showing the same pattern, it may be related either to matrix or a common preparation problem or error. If re-analysis gives the same result, a common error or matrix effect is suspected and the sample(s) is/are re-extracted and re-analyzed.

8.2.10.2 The following policy applies to re-extracted/reanalyzed samples:

- If the surrogates are within the QC limits, then an in-control situation has been demonstrated and only the second analysis is reported. The laboratory makes every attempt to re-extract samples within extraction holding times. If the re-extraction occurs beyond the hold time, then both the initial and the re-extracted results are reported on the samples.
- If the surrogates are still out-of-control, both the initial and re-extracted results are reported on the samples. An SDR must be completed and approved prior to the reporting of sample data.

8.2.11 Contamination in the Method Blank

If the MB is/appears to be contaminated with target compounds then the corrective action is documented in the Sample CAR. The decisions regarding the corrective action on a contaminated method blank are made using the following course of action:

- Reanalyze the MB on another instrument (one that has demonstrated a clean blank or sample).
- If contamination appears again, re-prepare the MB from the remaining extract. Analyze the re-prepared MB on the first instrument again.
- If the MB was found to be uncontaminated on the second instrument or after re-preparing (from the remaining extract) the source of contamination is a) in the first instrument or b) was introduced during the sample preparation just prior to analysis. Report only these results for the method blank.
- If upon repreparation/reanalysis, the MB is contaminated, the contamination was probably introduced during the extraction procedure. The level of corrective action is based on the concentration of the target compound contaminant(s) found in the MB. If the on-column amount for any target compound is greater than the reporting limit or greater than 5x the reporting limit for the phthalate ester, than the samples associated with this MB must be re-extracted.
- A situation may occur where the samples associated with a contaminated MB may not require re-extraction when the contaminating target compounds are not detected on the samples above the reporting limit which is approved by the supervisor or the section manager, the QA department, the Project Manager or the client.
- The re-extracted samples are reported as the initial analysis and the first extraction set need not be analyzed. The laboratory makes every attempt to re-extract samples within extraction holding times. If the re-extraction occurs beyond the hold time, then both the initial and the re-extracted results are reported on the samples.
- Any hold time violation requires that a Sample Discrepancy Report (SDR) be filled out and submitted to the project manager for approval before any results are reported.

8.2.12 LCS Recoveries

In-house QC limits from the analysis of the TCL BNA LCS spike (see Section 5.3) are generated annually. Upon identification of an out-of-control event in regards to LCS recoveries, the corrective action will be documented in the Sample CAR and the decision of whether to re-extract the associated samples is initialed and dated by the analyst. The sample reanalysis or re-extraction/reanalysis is also documented on the Sample CAR. This provides a documentation of a return to control or situation that requires addressing in the case narrative.

8.2.12.1 Only the spike recoveries of the 11 compounds found in Table 1 will be used to provide corrective action for out-of-control LCS recoveries. Certain clients require the control of the LCS recoveries using the full target compound list. If the LCS recovery is outside of the in-house QC limits, the following actions may be taken concerning reporting or re-extracting the associated samples:

- If there is a MS/MSD extracted on a sample in the same extraction set and the spike recoveries are acceptable within these samples, then the samples do not require re-extraction and the corrective action is addressed in the case narrative.
- If there was not a MS/MSD extracted in the same extraction set and the LCS/LCD recoveries are above the QC limits, then the associated samples require re-extraction only if the spike compounds are detected in the samples above the reporting limits.
- If there was a MS/MSD extracted in the same extraction set; the spike recoveries are outside of QC limits within these samples; and the LCS recovery was above the QC limits, then the associated samples require re-extraction only if the spike compounds are detected in the samples above the reporting limits.
- If the spike recoveries in the MS/MSD are outside of the QC limits and the LCS recovery was below the QC limits, then the samples associated with the LCS sample are re-extracted.
- Other situations where the LCS recovery is outside the QC limits will be evaluated on a case by case basis and the decision to re-extracted or report the associated sample will be made by the supervisor or section manager with the approval of the QA department, the Project Manager or the client.
- If the recovery in the LCS sample is outside of the QC limits, the LCS may be re-prepared using the remaining extract and reanalyzed on the same instrument or another instrument. If all recoveries are acceptable in the reanalysis, then the second analysis is reported as the initial analysis, the method is considered to be within control and the associated sample do not require re-extraction.

8.2.12.2 The following policies applies to samples re-extracted/reanalyzed due to out-of-control LCS spike recoveries:

- If the re-extraction occurs within the extraction holding times, then only the second analysis on the samples is reported. The laboratory makes every attempt to re-extract samples within extraction holding times.
- If the re-extraction occurs beyond the hold time, then both the initial and the re-extracted results are reported on the samples. An SDR must be completed and approved prior to the reporting of sample data.

All corrective action is documented on the Sample CAR with the decision whether to reanalyze the LCS or to re-extract all associated samples; initialed and dated by the analyst. The sample reanalysis is also documented on the Sample CAR.

8.2.13 Matrix Spike (MS) / MS Duplicate (MSD)

In MS/MSD analyses, the spike recoveries and RPD values (Table 1) function to illustrate and note possible matrix effects on the efficiency and completeness of analyte extraction. Out-of-control events on MS/MSD's are documented on the Sample CAR and initialed and dated by the analyst. Sample re-extraction is not performed due to out-of-control MS/MSD recoveries or RPD values; therefore, no return to control can be documented. The Sample CAR serves as a mechanism to address the out-of-control events in the case narrative. Corrective action in these situations is not used to suggest re-extraction. The corrective action decisions for out-of-control events on MS/MSD samples are driven by the acceptance/rejection of the LCS spike recovery. (Section 8.2.11).

8.2.14 Any other occurrences that require addressing in the case narrative are documented in either the CAR/Data Qualifications Report Logbook or on the Sample CAR and the corrective action is evaluated on a case by case basis.

8.2.15 Each instrument has a Maintenance Logbook. Major instrument maintenance and problem resolutions are documented in the maintenance logbook. The logbook provides for a description of the maintenance or repair performed and a corrective action for a return to control event, which is initialed and dated by the analyst.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Computer Data Production/Reduction

The HP ChemServer and Target software produces a Total Ion Chromatogram (TIC); quant report and background subtracted spectra of target analytes. For those clients requiring it, tentatively identified compound (TIC) searches are also performed. The data system will produce library search report, which includes unknown quantitation report and unknown mass spectra with the three TICs with the highest probability. All data for each sample is kept together.

9.2 Quantitation of Target Compounds

Quantitation of the target compounds and response factors are performed by the data system, but can be accomplished as follows:

9.2.1 Water Concentration (ug/L) = $\frac{(A_x)\,(I_s)\,(V_t)}{(A_{is})\,(RF)\,(V_o)\,(V_i)}$

Where:
A_x = area of characteristic ion for compound of interest
I_s = amount of internal standard injected (ng) (ISTD).
V_t = volume of total extract (uLs). This includes a measured final volume
A_{is} = area of characteristic ion of designated internal standard
RF = Average Response Factor from Initial Calibration

V_o = volume of water extracted (mLs)
V_i = volume of extract injected (uLs)

9.2.2 Soil, Sediment, Waste

$$\text{Concentration (ug/kg)} = \frac{(A_x)\,(I_s)\,(V_t)}{(A_{is})\,(RF)\,(V_i)\,(W_s)\,(D)}$$

All variables are the same as in the water calculation in Section 9.2.1 with the addition of the following:

W_s = weight of sample extracted or diluted (g)
D = (100 - % moisture in sample) / 100 (or 1 for wet weight basis)

A 2x dilution factor must be taken into account whenever the soil samples have undergone a GPC clean up.

NOTE: All dry weight corrections are made in LabNet at the time the final report is prepared.

9.2.3 Accuracy $\%R = \frac{(A_T - A_0)}{A_F} \times 100$

Where:
A_T = Total amount recovered in fortified sample
A_0 = Amount recovered in unfortified sample
A_F = Amount added to sample

9.2.4 Precision $\%D = \frac{|B_1 - B_2|}{B_1} \times 100$

$$RPD = \frac{|B_1 - B_2|}{(B_1 + B_2)/2} \times 100$$

Where:
B_1 = %Recovery MS (or LCS)
B_2 = %Recovered MSD (or LCD – when performed)

9.2.5 Quantitation by Method 8270C

The samples analyzed by Method 8270C will be quantitated using the initial calibration. For compounds that are calibrated using a linear regression curve, the following equation is used to determine the on-column amount of a compound:

Linear Regression Curve: $y = a_0 + (1/a_1)\,x$

Where:
$x = Area_{UNK}/Area_{ISTD}$
$y = Amount_{UNK}/Amount_{ISTD}$

The quantitation of compounds using either a linear regression is performed by the Target software and has been confirmed to be accurate to obtain the on-column $Amount_{UNK}$ of a target compound reported on the quantitation report. To obtain the final concentration the following equations are used:

Waters Concentration (µg/L) = $(Amount_{UNK})(V_t)/(V_o)(V_i)$

Soils Concentration (µg/L) = $(Amount_{UNK})(V_t)/(V_i)(W_s)(D)$

* The variables V_t, V_o, V_i, W_s, and D are defined in Section 9.2.1 and 9.2.2.

9.3 Quantitation of TIC's (Tentatively Identified Compounds)

Quantitation of TIC's is performed by the ChemServer system. The formulas above for waters and soils can be used with the following modifications. A_x and A_{is} should be taken from the unknown quantitation report produced by the data system. The nearest ISTD should be used. The RF is assumed 1. The concentration is therefore an estimate.

$$\text{Total ng of TIC} = \frac{\text{area of TIC x ng of its ISTD}}{\text{area of that ISTD}}$$

9.4 Operator Data Reduction/Review

The operator reviews the data and 1) makes judgments concerning the "realness" of those target compounds found and 2) makes judgments concerning the identification of the TICs and 3) modifies the output to confirm with those judgments to produce a data package reflective of those decisions. All initial data reduction/review is performed by the analyst in Target review of the Chemserver data system before any hardcopy reports are generated.

9.5 Initial Review

Operator determines that the analysis itself is acceptable. This means:

9.5.1 QC samples meet acceptable limits. See Section 8.2 for corrective action regarding sample analysis.

NOTE: Table 1 contains the laboratory's internally-derived statistical control limits for the MS/MSDs, the LCS, and the surrogates. The limits used to assess precision and

accuracy as well as the number of compounds being used for bench level control may vary with client, QAP, project, etc.. This information is transmitted to the bench via the COC: kick-off meetings, tech profiles, etc..

- Glassware blank (MB) is clean, ALL surrogates are within control limits. A clean MB means no target compounds above the reporting limit; except for the phthalates that must be less than 5x the reporting limit.
- All surrogates in the samples are within control limits or at most one surrogate in each fraction is out. No surrogate can be <10%. All surrogates must be within control limits for all MBs.
- All MS/MSD and LCS recoveries are within in-house generated control limits specified in Table 1 for the spike compounds in the HSL BNA LCS spike identified in Section 5.3.

9.5.2 The sample does not require any further dilutions or analysis at a more concentrated level. Visually confirm complete integration for any large and/or saturated target compound found. Dilutions are made to keep the target compounds in the upper half of the calibration range. MS/MSD or LCS samples are never diluted to get spiked or non-spiked analytes within the calibration range.

9.5.2.1 The sample does not require re-analysis for any other reason (i.e., leak, analysis past tune time, ISTD areas low, etc..)

9.5.2.2 Identification of target compounds. The following criteria are used in the positive identification of target compounds. **These are guidelines, they are not absolute.**

- "elution of component at the same relative retention time as the standard component."

The elution times should compare within 0.06 min. The standard MUST be run on the same 12-hour period as the sample. If co-eluting analytes interfere with comparisons of retention times, other ions characteristic to that compound can be used to confirm relative retention times.

- "correspondence of the sample component and standard component mass spectrum."

All ions present in the standard spectrum at a 10% relative intensity (most abundant ion being 100%) MUST be present in the sample.

The relative intensities of the above ions must agree within ±20%, between the standard and sample. If an ion has 50% intensity in the standard, the corresponding ion must be between 30% and 70% in the sample.

Ions >10% in the sample but not present in the standard must be considered and accounted for.
If a compound cannot be verified by the above, **but in the operator's technical judgment, the ID is correct**, it is reported as such.

9.5.2.3 Once all positive identification is made, the file is modified to reflect these decisions. All analytes at concentrations less than the reporting limit are automatically flagged with a 'J'.

9.5.2.4 Identification of TIC's

In general, up to as many as 20 non-target compounds are tentatively identified by the data system and operator. The data system provides the operator with a subtracted mass spectrum of the unknown and the mass spectra of the first 3 matches. Molecular formulas, molecular weights, and CAS #'s are included. The following **guidelines** are used:

9.5.2.4.1 Relative intensities of major ions in the reference spectrum should be present in the sample (ions >10%).

- Relative ions should agree within ±20%.
- Molecular ions in the reference should be in the samples.
- Review the possibility of background and/or co-eluting compounds for those ions present in the sample but not in the standard.
- If ions are present in the sample but not in the standard, review the possibility of the presence of background or co-eluting compounds.
- If ions are present in the standard but not in the sample, review the possibility that the ions were subtracted out because they are also common to the background or co-eluting compounds.
- In the event no valid interpretation can be made, the compound is called "unknown".
- Interpretation can be often narrowed down to a class of compounds, molecular formula, or weight.

9.6 Manual Integration Policy

In each case where the file has been edited or manual integrations have been performed the operator must identify, initial, and date the changes on the hardcopy report. The following guidelines apply:

- Manual integrations should be consistent between all files integrated.
- Manual integrations should not be performed to meet QC criteria.
- Manual integrations are automatically flagged with an 'M' on the raw data.
- Excessive manual integrations may reflect an instrumental or methodological problem that should be addressed.

- Manual integrations shall follow the STL Corporate SOP for manual integrations (#S-Q-004) located in Attachment 11. An example of one such integration and documentation is included in the attachment.

Manual integrations are most often performed for the following reasons:

- Assignment of correct peak that was mis-identified by the data system.
- Incomplete auto-integration due to high level of target compound detected.
- Incomplete auto-integration due to background interference.
- Incorrect auto-integration due to co-elution or near co-elution of compounds.
- Missed peaks.

The analysts review all integrations. Spectra and Extracted Ion Chromatography Profiles (EICP) are printed after any integration takes place for target compounds and are routinely included in the data packages. If EICP's for internal standards, surrogates and calibration standards are required to satisfy client deliverables, they can be provided, but will not be routinely added. Manual integrations may be documented in the case narrative if so required, however, references to this SOP will be used for explanations, and any further documentation beyond initials and dates will not be performed.

9.7 Final Review

Once 1) the analysis is determined to be acceptable and 2) the initial review and data reduction has occurred 3) all forms are produced using the Envision data packaging software and the package is put together 4) the results transferred to LabNet and 5) the package is put together and submitted for it's first 100% review. The checklist in Attachment 9 is used as an aid to review.

Upon the first 100% review, the review checklist is initialed and dated as reviewed. The package, with its review sheet, comments, and any C/A forms is submitted to the supervisor or section manager for a second review and validation.

The entire sample tracking system can be summarized in Attachment 10. The complete analysis scheme can be summarized in Sections 7.1.1, 7.1.2 and in Attachment 10.

10.0 Waste Management and Pollution Prevention

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out:

- Waste from this procedure will enter the Methylene Chloride (DCM) waste stream.
- Expired and single component standards will be turned over to the EHSC or Waste Technician.

11.0 Method Performance Criteria

Refer to Sections 1, 6, 7 and 8.

12.0 References

Refer to Sections 1.0.

13.0 Attachments

Table 1: Example: Reporting Limits (RLs); Internal Statistical Control Limits for MS/MSDs, LCSs, Surrogates for Water and Soil/Sediment Samples
Table 2: Characteristic Ions for Semi-Volatile Organic Compounds
Table 3: Internal Standards with Corresponding Analysts Assigned for Quantitation.
Table 4: DFTPP Key Ions and Ion Abundance Criteria
Table 5: Calibration Check Compounds and System Performance Check Cmpds.

Attachment 1: Example: DFTPP Method
Attachment 2: STL Corporate Procedure, P-T-001, 'Selection of Calibration Points'
Attachment 3: Example: BNA Method for Standards and Samples
Attachment 4: Example: Instrument Generated Initial Calibration - Form 6
Attachment 5: Example: Acceptable Initial Calibration - Form 6
Attachment 6: GC/MS Calibration - Evaluation and Acceptance Criteria
Attachment 7: Example: Semi-Volatile Analysis Logbook
Attachment 8: Example: Sample Corrective Action Report
Attachment 9: Example: Data review checklist
Attachment 10: Example: Analysis Scheme and Sample Tracking Flowcharts
Attachment 11: STL Corporate SOP, S-Q-004, 'Acceptable Manual Integration Practices and example documentation.

Appendix A: Requirements for DOD QSM Version 3.0

SOP No.	Revision No.	Date	Page
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Historical File:

Revision 00: 08/03/90
Revision 01: 11/22/91
Revision 02: 03/22/93
Revision 03: 10/31/95
Revision 04: 04/09/96
Revision 05: 04/10/97
Revision 06: 06/13/97
Revision 07: 02/11/98
Revision 08: 01/29/99
Revision 09: 07/01/99
Revision 10: 09/12/00
Revision 11: 02/07/02
Revision 12: 08/12/03
Revision 13: 11/05/04
Revision 14: 11/2/05

Reason for Change; Revision 14:

- Annual Review
- Deleted all references to power curve.
- Deleted DFTPP method attachment
- Updated RT's of compounds in Table 2
- Added all SOP Change Forms
- Updated Section 1.0 to include DoD QSM reference.
- Added Appendix A: DoD QSM Requirements Table

U:\QC\SOP\MB\UMB-8270.DOC

Table 1.

Example: Reporting Limits (RLs); Internal Statistical Control Limits for MS/MSDs, LCSs, Surrogates for Water and Soil/Sediment Samples

- RLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, RLs will be higher based on the percentage moisture in each sample. Normally, GPC clean-up is NOT performed on any samples. Upon GPC clean-up, the RL listed would be 2x greater than normally reported.
- Sample RLs are highly matrix-dependent. The RLs listed herein are provided for guidance and may not always be achievable.
- Statistical control limits and MDLs are determined annually and are subject to change. Contact the laboratory for the latest values.

Table 2. Characteristic Ions for Semi-Volatile Organic Compounds

Compound	Approx. Retention Time (Min)	Primary Ion	Secondary Ion(s)
Acenaphthene	8.58	154	153, 152
Acenaphthene-d_{10} (I.S.)	8.54	164	162, 160
Acenaphthylene	8.37	152	151, 153
Acetophenone	5.66	105	77, 51
2-Acetylaminofluorene	12.22[a]	181	180, 182, 223
Aniline	4.94	93	66, 65
Anthracene	10.19	178	176, 179
4-Aminobiphenyl	9.99[a]	169	168, 170
Aramite	11.5[a]	63	185, 191, 187
Benzidine	11.30	184	92, 185
Benzoic Acid	6.32	122	105, 77
Benzo(a)anthracene	12.39	228	229, 226
Benzo(b)fluoranthene	13.38	252	253, 125
Benzo(k)fluoranthene	13.40	252	253, 125
Benzo(g,h,i)perylene	15.71	276	138, 277
Benzo(a)pyrene	13.74	252	253, 125
Benzyl alcohol	5.37	108	79, 77
Bis(2-chloroethoxy)methane	6.31	93	95, 123
Bis(2-chloroethyl)ether	4.99	93	63, 95
2,2'-oxybis(1-Chloropropane)	5.53	45	77, 121
Bis(2-ethylhexyl)phthalate	12.37	149	167, 279
4-Bromophenyl phenyl ether	9.66	248	250, 141
Butylbenzylphthalate	11.92	149	91, 206
sec-Butyl-4,6-dinitrophenol	10.24	211	212, 240, 163
4-Chloroaniline	6.67	127	129
Chlorobenzilate	11.88	139	251, 253, 141
2-Chloronaphthalene	7.90	162	127, 164
4-Chloro-3-methylphenol	7.71	107	144, 142
2-Chlorophenol	5.05	128	64, 130
4-Chlorophenyl phenyl ether	9.13	204	206, 141
Carbazole	10.34	167	166, 139
Chrysene	12.42	228	226, 229
Chrysene-d_{12} (I.S.)	12.40	240	120, 236
Diallate	9.65	43	86, 234
Dibenz(a,h)anthracene	15.27	278	139, 279
Dibenzofuran	8.76	168	139
Di-n-butylphthalate	10.67	149	150, 104
1,3-Dichlorobenzene	5.20	146	148, 111
1,4-Dichlorobenzene	5.25	146	148, 111
1,4-Dichlorobenzene-d_4 (I.S.)	5.23	152	150, 115
1,2-Dichlorobenzene	5.44	146	148, 111
3,3'-Dichlorobenzidine	12.35	252	254, 126
2,4-Dichlorophenol	6.42	162	164, 98
2,6-Dichlorophenol	6.67[a]	162	164, 98
3,3'-Dimethylbenzidine	12.00	212	211, 213, 196
meta-Dinitrobenzene	8.34	168	76, 75, 92
1,4-Dioxane	2.68	88	58, 87
Diethylphthalate	9.06	149	177, 150

Table 2. Characteristic Ions for Semi-Volatile Organic Compounds

Compound	Approx. Retention Time (Min)	Primary Ion	Secondary Ion(s)
p-Dimethylaminoazobenzene	11.56[a]	120	225, 77
7,12-Dimethylbenz(a)anthracene	13.50[a]	256	241, 257
a,a-Dimethylphenethylamine	6.60[a]	58	91, 42
2,4-Dimethylphenol	6.19	122	107, 121
Dimethylphthalate	8.27	163	194, 164
4,6-Dinitro-2-methylphenol	9.25	198	51, 105
2,4-Dinitrophenol	8.62	184	63, 154
2,4-Dinitrotoluene	8.79	165	63, 89
2,6-Dinitrotoluene	8.35	165	63, 89
Diphenylamine	9.24[a]	169	168, 167
1,2-Diphenylhydrazine	9.31	77	105, 182
Di-n-octylphthalate	12.88	149	167, 43
Ethyl Methanesulfonate	3.66[a]	79	109, 97
Fluoranthene	11.22	202	101, 203
Fluorene	9.12	166	165, 167
2-Fluorobiphenyl (surr.)	7.78	172	171
2-Fluorophenol (surr.)	4.04	112	64
Hexachlorobenzene	9.82	284	142, 249
Hexachlorobutadiene	6.78	225	223, 227
Hexachlorocyclopentadiene	7.60	237	235, 272
Hexachloroethane	5.76	117	201, 199
Hexachlorophene	13.60	196	198, 209, 406
Hexachloropropene	6.73	213	215, 211, 143
Indeno(1,2,3-cd)pyrene	15.28	276	138, 227
Isophorone	6.09	82	95, 138
Isosafrole	7.75	162	161, 131, 78
Methapyrilene	11.22[a]	58	97, 72, 191
3-Methylcholanthrene	15.12[a]	268	253, 267
Methyl Methanesulfonate	3.55[a]	80	79, 65
2-methylnaphthalene	7.35	142	141
2-Methylphenol (o-cresol)	5.49	108	107, 79
4-Methylphenol (m&p-cresol)	5.63	108	107, 79
Naphthalene	6.60	128	129, 127
Naphthalene-d_8 (I.S.)	6.58	136	68
1,4-Naphthoquinone	8.33[a]	158	130, 104, 102
1-Naphthylamine	8.77[a]	143	115, 116
2-Naphthylamine	8.99[a]	143	115, 116
2-Nitroaniline	8.03	65	92, 138
3-Nitroaniline	8.50	138	108, 92
4-Nitroaniline	9.20	138	108, 92
Nitrobenzene	5.85	77	123, 65
Nitrobenzene-d_5 (surr.)	5.82	82	128, 54
2-Nitrophenol	6.18	139	109, 65
4-Nitrophenol	8.66	139	109, 65
5-Nitro-o-toluidine	9.24	77	152, 106, 79
4-Nitroquinoline-1-oxide	11.25	190	160, 128, 89
N-Nitroso-di-n-butylamine	7.15[a]	84	57, 41
N-Nitrosodimethylamine	2.97	42	74, 44
N-Nitrosodiethylamine	4.27	42	102, 56, 57

Table 2. Characteristic Ions for Semi-Volatile Organic Compounds

Compound	Approx. Retention Time (Min)	Primary Ion	Secondary Ion(s)
N-Nitrosodiphenylamine	9.28	169	168, 167
N-Nitrosodi-n-propylamine	5.68	70	42, 101, 130
N-Nitrosomethylethylamine	3.67	42	88, 43, 56
N-Nitrosomorpholine	5.88	56	88, 43, 56
N-Nitrosopiperidine	5.94	42	116, 86
N-Nitrosopyrrolidine	5.66	100	41, 68
Pentachlorobenzene	8.79[a]	250	252, 248
Pentachloronitrobenzene	9.78[a]	295	237, 142
Pentachlorophenol	9.99	266	264, 268
Perylene-d_{12} (I.S.)	13.79	264	260, 265
Phenacetin	9.63[a]	108	109, 179
Phenanthrene	10.15	178	179, 176
Phenanthrene-d_{12} (I.S.)	10.12	188	94, 80
Phenol	4.89	94	65, 66
Phenol-d_5 (surr.)	4.88	99	42, 71
p-Phenylenediamine	7.44	108	80, 52, 54
2-Picoline	3.25[a]	93	66, 92
Pronamide	9.87[a]	173	175, 145
Pyrene	11.41	202	200, 203
Pyridine	2.97	79	52, 51
Safrole	7.24	162	161, 131, 104
Terphenyl-d_{14} (surr.)	11.52	244	122, 212
1,2,4,5-Tetrachlorobenzene	7.58[a]	216	214, 218
2,3,4,6-Tetrachlorophenol	8.85[a]	232	230, 131
2,4,6-Tribromophenol (surr.)	9.43	330	332, 141
1,2,4-Trichlorobenzene	6.53	180	182, 145
2,4,5-Trichlorophenol	7.73	196	198, 200
2,4,6-Trichlorophenol	7.69	196	198, 200
o-Toluidine	5.90	106	107, 77, 56
Sym-Trinitrobenzene	9.87	75	213, 74

Table 3.

Internal Standards with Corresponding Analytes Assigned for Quantitation. (Listed in order of elution)

(1) 1,4-Dichlorobenzene-d_4	(2) Naphthalene-d_8	(3) Acenaphthene-d_{10}
1,4-Dioxane	n-Nitrosopiperidine	1,2,4,5-Tetrachlorobenzene
n-Nitrosodimethylamine	Nitrobenzene-d5*	Isosafrole
Pyridine	Nitrobenzene	Hexachlorocyclopentadiene
2-Picoline	Isophorone	1,4-Naphthoquinone
n-Nitrosomethylethylamine	Hexachloropropene	2,4,6-Trichlorophenol
Methyl Methanesulfonate	a,a-Dimethylphenethylamine	2,4,5-Trichlorophenol
n-Nitrosodiethylamine	2,6-Dichlorophenol	meta-Dinitrobenzene
2-Fluorophenol*	2-Nitrophenol	2-Fluorobiphenyl*
Ethyl Methanesulfonate	2,4-Dimethylphenol	2-Chloronaphthalene
Aniline	bis(2-Chloroethoxy)methane	2-Nitroaniline
Phenol-d5*	2,4-Dichlorophenol	Pentachlorobenzene
Phenol	Benzoic acid	1-Naphthylamine
bis(2-Chloroethyl)ether	1,2,4-Trichlorobenzene	Dimethylphthalate
2-Chlorophenol	n-Nitrosodi-N-Butylamine	2,6-Dinitrotoluene
n-Nitrosopyrrolidine	Naphthalene	Acenaphthylene
Acetophenone	P-Phenylenediamine	2,3,4,6-Tetrachlorophenol
1,3-Dichlorobenzene	4-Chloroaniline	2-Naphthylamine
o-Toluidine	Hexachlorobutadiene	3-Nitroaniline
n-Nitrosomorpholine	Safrole	Acenaphthene
1,4-Dichlorobenzene	4-Chloro-3-methylphenol	2,4-Dinitrophenol
1,2-Dichlorobenzene	2-Methylnaphthalene	Dibenzofuran
Benzyl alcohol		4-Nitrophenol
2-Methylphenol		2,4-Dinitrotoluene
o-Cresol		Diethylphthalate
2,2'-oxybis(1-Chloropropane)		Fluorene
N-Nitroso-di-n-propylamine		4-Chlorophenyl-phenylether
4-Methylphenol		4-Nitroaniline
meta & para-Cresol		1,2-Diphenylhydrazine
Hexachloroethane		2,4,6-Tribromophenol*

(4) Phenanthrene-d_{10}	(5)Chrysene-d_{12}	(6)Perylene-d_{12}
5-Nitro-o-Toluidine	Aramite	7,12-Dimethylbenz(a)anthracene
Diphenylamine	P-Dimethylaminoazobenzene	Hexachlorophene
Diallate	Chlorobenzilate	Di-n-octylphthalate
Sym-Trinitrobenzene	Benzidine	Benzo(b)fluoranthene
Phenacetin	Pyrene	3-Methylcholanthrene
4,6-Dinitro-2-methylphenol	3,3'-Dimethylbenzidine	Benzo(k)fluoranthene
n-Nitrosodiphenylamine	Terphenyl-d14*	Benzo(a)pyrene
Pentachloronitrobenzene	2-Acetylaminofluorene	Indeno(1,2,3-cd)pyrene
4-Aminobiphenyl	Butylbenzylphthalate	Dibenzo(a,h)anthracene
Pronamide	Benzo(a)anthracene	Benzo(g,h,i)perylene
2-Sec-Butyl-4,6-Dinitrophenol	3,3'-Dichlorobenzidine	
4-Bromophenyl-phenylether	Chrysene	
Hexachlorobenzene	bis(2-Ethylhexyl)phthalate	
Pentachlorophenol		
Phenanthrene		* Surrogate Compounds
Anthracene		
Carbazole		
4-Nitroquinoline-1-Oxide		
Methapyrilene		
Di-n-butylphthalate		
Fluoranthene		

Table 4. DFTPP Key Ions and Ion Abundance Criteria[a]

Mass	Ion Abundance Criteria
51	30 - 60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40 - 60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5 - 9% of mass 198
275	10 - 30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17 - 23% of mass 442

[a]J.W. Eichelberger, L.E. Harris, and W.L. Budde. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry", Analytical Chemistry, 47, 995 (1975).

Table 5. Calibration Check Compounds (CCCs) and System Performance Check Cmpds. (SPCCs)*

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	2,4-Dinitrophenol*
N-Nitroso-di-n-propylamine*	4-Nitrophenol*
Hexachlorocyclopentadiene*	

Attachment 1.

Example: DFTPP Method

1. GC Oven Parameters

Temp. (°C)	Hold Time (min.)	Ramp Rate (°C/min.)
160	4	8
220	Until Benzidine elutes	

2. GC Electronic Pressure Control (EPC) Parameters

Split Flow	15.0 mL / minute
Split Ratio	15:1
Split / Splitless Time	0.75 minutes
Constant Flow	1.0 mL / minute

3. Mass Spectrometer Parameters

Scan Range	35 – 500 m/z
Threshold	150
A/D Ratio	4
Scan / Second	2
Solvent Delay (scan start time):	~5.0 minutes (before the elution of Pentachlorophenol).
Run Time (scan stop time)	~15.0 minutes (after the elution of Benzidine).

Attachment 2.

Example: STL Corporate Procedure, P-T-001, 'Selection of Calibration Points'

Approvals and Signatures

Senior Vice President & Chief Operating Officer:	Dr. Keith C. Wheatstone	Date: 10/6/2004
Vice President, Client and Operations Services:	Dr. Charles W. Carter	Date: 10/6/2004
Technology Director:	Dr. Richard Burrows	Date: 9/8/2004

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1.0 PURPOSE

This policy describes Severn Trent Laboratories (STL) requirements for determination of the number of points, and removal of points from calibration curves.

2.0 SCOPE

Applies to all multi-level initial calibrations.

3.0 POLICY

3.1 If the number of data points required for an initial calibration is defined in the method, Quality Assurance (QA) plan, published report, or previously approved Standard Operating Procedure (SOP) that is what will be used.

3.2 In the cases not defined in Section 1, the number of data points will be determined by the technical director based on the Data Quality Objectives (DQOs) for precision and accuracy to be met by the method.

Examples:

A. Need to analyze a new pesticide in water and a published method does not exist. The data will be used to screen samples by UV-HPLC at a waste site for further remediation, using DQOs that require precision/accuracy of ± 50%.

The Technical director selects 2 data points to represent the range of the expected concentration of pesticide and based on 4 Laboratory Control Samples (LCS), the recoveries ranged from 78-104%. Therefore, 2 data points are sufficient for initial calibration for this method.

NOTE: Calibration curves with less than 3 points should only be used after discussion with the client that the data quality objectives will be met.

B. Same compound as above but being measured in laboratory for meeting regulatory limit of 0.05 mg/L in water. Precision and accuracy of ± 20% required.

A five-point calibration is used, based on similar requirements in published methods with similar objectives and the high level of precision and accuracy required.

As noted above for methods where technical director selects the number of data points to meet DQOs for precision and accuracy, the 4 LCS used in the demonstration of capability will be used to assure those DQOs are met. The SOP will then be approved by the Quality Assurance (QA) Manager.

3.3 Removal of Points from a Calibration Curve

3.3.1 Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted unless an injection or instrument problem confined to that point can be clearly documented as described below. Removal of points for individual analytes from levels other than the highest and lowest is not permitted in any event.

3.3.2 If the analyst can document that a level is not valid because of an injection or instrument problem confined to that run, the level may be excluded if the curve still has sufficient levels, or the run may be repeated once only. The whole level (all compounds) must be

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removed or replaced. The curve is evaluated with the level removed or replaced. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve reanalyzed. Corrective action may include, but is not limited to, instrument maintenance and/or re-preparation of standards.

3.3.3 One of the following conditions must be satisfied to allow removal or replacement of a level:

- The data file is corrupted and unusable or the run is interrupted before completion.
- The analyst observes and documents a problem such as leaking of a purge vessel.
- For internal standard methods, the recovery of the internal standards is less than 70% or greater than 130% of the recovery in the other standards, or the amount of analyte recovered is less than 70% or greater than 130% of the expected values (indicating an improperly made up standard).
- For external standard methods, the unit response of the analyte is less than 70% or greater than 130% of the average unit response for the analyte in the other calibration standards (indicating an improperly prepared standard or bad injection).

3.3.4 When using autosamplers with discrete sample pathways for different samples (such as 16 port purge and trap autosamplers) the level to be replaced must be reanalyzed on the same port or that port must be excluded from sample analysis until corrective action is performed and verified by successful analysis of a continuing calibration standard on that port.

3.3.5 The reason for replacing the level **must** be documented in the run log. The fact that the curve passes criteria with the level removed is **not** alone sufficient evidence to document an injection or instrument problem confined to the level.

3.3.6 Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed then the reporting limit is raised to be equivalent to the lowest level used in the calibration curve. In any event the number of levels remaining in the calibration must be at least that required by the method.

3.3.7 Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method.

4.0 RESPONSIBILITIES

All STL associates utilizing methods involving multi-point calibrations are required to follow this policy.

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5.0 ATTACHMENTS

Not Applicable.

6.0 REVISION HISTORY

Revision 3: Updated by Richard Burrows, Technology Director; 9/8/2004.
Section 3.2: Amended 'NOTE'.
Section 3.3.3, bullet #4, text reworded for clarification.

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Attachment 3.

Example: BNA Method for Standards and Samples

1. GC Oven Parameters

Initial Temp.	40°C
Initial Time	1.0 min.

Ramp Rate (°C / min.)	Final Temp. (°C)	Final Time (min.)
22	220	0
35	325	4.5

2. GC Electronic Pressure Control (EPC) Parameters

Constant Flow:	2.0 mL / minute

3. Mass Spectrometer Parameters

Scan Range:	35 - 500 m/z
Threshold:	150
A/D Ratio:	4
Scan/second:	2
Solvent Delay (scan start time):	Before the elution of the first compound
Run Time (scan stop time):	Until after the elution of last compound

Attachment 4.

Example: Instrument Generated Initial Calibration - Form 6

INITIAL CALIBRATION DATA

Start Cal Date : 11-FEB-2005 15:50
End Cal Date : 11-OCT-2005 21:46
Quant Method : ISTD
Origin : Disabled
Target Version : 3.50
Integrator : HP RTE
Method file : /var/chem/gcl1.i/1011-8270-1.b/8270-1.m
Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Calibration File Names:
Level 1: /var/chem/gcl1.i/1011-8270-1.b/1i1011k.d
Level 2: /var/chem/gcl1.i/1011-8270-1.b/1i1011j.d
Level 3: /var/chem/gcl1.i/1011-8270-1.b/1i1011i.d
Level 4: /var/chem/gcl1.i/1011-8270-1.b/1i0211i.d
Level 5: /var/chem/gcl1.i/1011-8270-1.b/1i1011g.d
Level 6: /var/chem/gcl1.i/1011-8270-1.b/1i1011f.d
Level 7: /var/chem/gcl1.i/1011-8270-1.b/1i1011e.d
Level 8: /var/chem/gcl1.i/1011-8270-1.b/1i1011d.d
Level 9: /var/chem/gcl1.i/1011-8270-1.b/1i1011c.d
Level 10: /var/chem/gcl1.i/1011-8270-1.b/1i1011b.d
Level 11: /var/chem/gcl1.i/1011-8270-1.b/1i1011a.d

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
1 2-Ethoxyethanol	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
2 1,4-Dioxane	+++++	+++++	+++++	+++++	+++++	0.36019			
	0.26608	0.28900	0.38944	0.29487	0.28186		0.31357	15.716	<-
3 n-Nitrosodimethylamine	+++++	+++++	+++++	+++++	0.32168	0.63849			
	0.58675	0.39146	0.28181	0.44834	0.44517		0.44481	29.347	<-
4 Pyridine	+++++	+++++	+++++	+++++	+++++	1.21855			
	1.08943	0.70783	0.53256	0.79263	0.77250		0.85225	29.841	<-
5 2-Picoline	+++++	+++++	+++++	+++++	0.96160	0.80315			
	0.66736	0.71247	1.04592	0.96812	0.75595		0.84494	17.281	<-
6 n-Nitrosomethylethylamine	+++++	+++++	+++++	+++++	0.71704	0.65726			
	0.66636	0.77562	0.76482	0.82198	0.81740		0.74578	9.021	

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Target Version : 3.50
Integrator : HP RTE
Method file : /var/chem/gcl1.i/1011-8270-1.b/8270-1.m
Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
7 Methyl Methanesulfonate	+++++	+++++	+++++	+++++	0.21604	0.20209			
	0.19518	0.21562	0.22853	0.21179	0.16045		0.20424	10.802	
9 n-Nitrosodiethylamine	+++++	+++++	+++++	+++++	0.66320	0.66703			
	0.70632	0.40800	0.66425	0.70422	0.69968		0.64467	16.466	<-
10 Ethyl Methanesulfonate	+++++	+++++	+++++	+++++	0.80097	0.74438			
	0.72168	0.81514	0.79240	0.75733	0.74947		0.76877	4.462	
11 Acrylamide	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
12 Camphene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
13 Benzenethiol	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
15 Phenol	+++++	+++++	+++++	+++++	1.22547	1.30767			
	1.33057	1.21082	1.18773	1.26029	1.19555		1.24544	4.489	
16 Aniline	+++++	+++++	+++++	+++++	1.15139	1.23674			
	1.22975	1.12370	1.11341	1.08973	1.03569		1.14006	6.398	
17 Pentachloroethane	+++++	+++++	+++++	+++++	0.59415	0.60288			
	0.54396	0.59425	0.60120	0.61818	0.62404		0.59695	4.358	
18 bis(2-Chloroethyl)ether	+++++	+++++	+++++	+++++	1.03129	1.01782			
	1.06155	0.97346	0.94249	1.09734	1.12241		1.03519	6.221	

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Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	___ RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
19 2-Chlorophenol	+++++	+++++	+++++	+++++	1.06030	1.08284			
	1.08288	1.01741	0.98293	1.03143	1.02516		1.04042	3.541	
20 n-Decane	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
21 1,3-Dichlorobenzene	+++++	+++++	+++++	+++++	1.31606	1.35659			
	1.27472	1.19167	1.19345	1.25462	1.15605		1.24902	5.827	
23 1,4-Dichlorobenzene	+++++	+++++	+++++	+++++	1.39555	1.34766			
	1.10024	1.50886	1.56984	1.46801	1.69911		1.44132	13.147	
24 n-Nitrosomorpholine	+++++	+++++	+++++	+++++	+++++	0.62424			
	0.58631	0.63892	0.56895	+++++	0.46613		0.57691	11.791	
25 Benzyl alcohol	+++++	+++++	+++++	+++++	0.51516	0.63495			
	0.69966	0.66092	0.66026	0.72965	0.71718		0.65968	10.948	
26 1,2-Dichlorobenzene	+++++	+++++	+++++	+++++	1.32637	1.31021			
	1.21300	1.24857	1.24755	1.25588	1.24926		1.26441	3.133	
27 Indene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
28 o-Cresol	+++++	+++++	+++++	+++++	0.99854	0.98575			
	1.02797	0.95407	0.96586	1.04061	1.01535		0.99831	3.201	
29 2-Methylphenol	+++++	+++++	+++++	+++++	0.99854	0.98575			
	1.02797	0.95407	0.96586	1.04061	1.01535		0.99831	3.201	

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Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	___ RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
30 2,2'-oxybis(1-Chloropropane)	+++++	+++++	+++++	+++++	2.42492	2.41438			
	2.49621	2.32365	2.28822	2.33338	2.31777		2.37122	3.166	
31 meta & para-Cresol	+++++	+++++	0.73415	+++++	0.89951	1.07477			
	1.04132	0.98431	0.94526	1.04364	0.99560		0.96482	11.309	
32 4-Methylphenol	+++++	+++++	0.73415	+++++	0.89951	1.07477			
	1.04132	0.98431	0.94526	1.04364	0.99560		0.96482	11.309	
33 N-Nitroso-di-n-propylamine	+++++	0.70567	0.94144	+++++	0.81061	0.85510			
	0.86041	0.80683	0.79028	0.82851	0.82719		0.82512	7.631	
34 Aldicarb	+++++	+++++	+++++	+++++	0.18249	0.10908			
	0.07725	0.15540	0.05339	0.07566	0.05753		0.10154	49.283	<-
35 o-Toluidine	+++++	+++++	+++++	+++++	1.64473	1.55348			
	1.44009	1.57777	1.54762	1.48188	1.53650		1.54029	4.274	
36 Hexachloroethane	+++++	+++++	+++++	+++++	0.58130	0.56195			
	0.58296	0.54580	0.54571	0.54437	0.54598		0.55830	3.112	
38 Nitrobenzene	+++++	+++++	0.34738	+++++	0.39476	0.37554			
	0.36423	0.35984	0.36843	0.45232	0.44143		0.38799	10.022	
39 n-Nitrosopiperidine	+++++	+++++	+++++	+++++	0.28288	0.29013			
	0.27707	0.27769	0.28167	0.29185	0.28405		0.28362	1.998	
40 Isophorone	+++++	+++++	+++++	+++++	0.61208	0.59466			
	0.60221	0.59679	0.59851	0.62766	0.61720		0.60702	2.027	

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Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	___ RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
41 a,a-Dimethylphenethylamine	+++++	+++++	+++++	+++++	+++++	+++++			
	0.12565	0.14474	0.13024	0.16764	0.24109		0.16187	29.165	<-
42 2-Nitrophenol	+++++	+++++	+++++	+++++	0.17196	0.17291			
	0.17034	0.17088	0.17557	0.19110	0.18637		0.17702	4.684	
43 Benzal Chloride	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
44 2,4-Dimethylphenol	+++++	+++++	+++++	+++++	0.30955	0.31102			
	0.32008	0.30210	0.29395	0.32625	0.31680		0.31139	3.517	
45 bis(2-Chloroethoxy)methane	+++++	+++++	+++++	+++++	0.38143	0.37289			
	0.36498	0.36125	0.36993	0.37389	0.36551		0.36998	1.833	
46 Benzoic acid	+++++	+++++	+++++	+++++	+++++	0.14215			
	0.17057	0.16106	0.15482	0.22363	0.21643		0.17811	18.994	<-
47 Acetophenone	+++++	+++++	+++++	+++++	1.53795	1.53181			
	1.59005	1.47108	0.96511	1.49801	1.48332		1.43962	14.797	
48 2,6-Dichlorophenol	+++++	+++++	+++++	+++++	0.28660	0.28253			
	0.27340	0.25730	0.25466	0.27367	0.25953		0.26967	4.699	
49 n-Nitrosopyrrolidine	+++++	+++++	+++++	+++++	0.49590	0.57126			
	0.57571	0.52590	0.51153	0.56645	0.55318		0.54285	5.836	
50 1,2,4-Trichlorobenzene	+++++	+++++	+++++	+++++	0.34675	0.34303			
	0.34122	0.33508	0.34232	0.36191	0.35104		0.34591	2.485	

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Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	___ RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
52 Naphthalene	+++++	+++++	1.01872	+++++	0.86549	0.85686			
	0.83708	0.82093	0.83416	0.86198	0.84044		0.86696	7.288	
53 p-Phenylenediamine	+++++	+++++	+++++	+++++	+++++	+++++			
	0.24796	0.30398	0.35075	+++++	0.30012		0.30070	13.974	
54 2,4-Dichlorophenol	+++++	+++++	+++++	+++++	0.28445	0.29462			
	0.28441	0.26128	0.26399	0.28994	0.27530		0.27914	4.568	
55 4-Chloroaniline	+++++	+++++	+++++	+++++	0.32523	0.33199			
	0.31033	0.28762	0.27632	0.29322	0.26972		0.29921	8.002	
56 Hexachloropropene	+++++	+++++	+++++	+++++	0.29991	0.30707			
	0.29192	0.29101	0.28477	0.30191	0.29729		0.29627	2.547	
57 Hexachlorobutadiene	+++++	+++++	+++++	+++++	0.23917	0.23179			
	0.23310	0.23559	0.23829	0.24620	0.24032		0.23778	2.046	
58 Quinoline	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
59 n-Nitrosodi-N-Butylamine	+++++	+++++	+++++	+++++	0.22427	0.21074			
	0.21402	0.20733	0.20961	0.22650	0.21817		0.21581	3.441	
60 4-Chloro-3-methylphenol	+++++	+++++	+++++	+++++	0.26679	0.27384			
	0.24755	0.23074	0.21621	0.23632	0.22508		0.24236	8.863	
61 Safrole	+++++	+++++	+++++	+++++	0.23873	0.22961			
	0.22925	0.26289	0.24148	0.23707	0.23106		0.23858	4.917	

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Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
62 2-Methylnaphthalene	+++++	0.47461	0.64443	+++++	0.83777	0.82869			
	0.80122	0.76208	0.75597	0.79910	0.77425		0.74201	15.521	<-
63 Phthalic Anhydride	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
64 1-Methylnaphthalene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
65 Hexachlorocyclopentadiene	+++++	+++++	+++++	+++++	0.45371	0.47635			
	0.48317	0.48230	0.46695	0.48798	0.49463		0.47787	2.879	
66 1,2,4,5-Tetrachlorobenzene	+++++	+++++	+++++	+++++	0.68586	0.67747			
	0.67289	0.67399	0.68905	0.65823	0.66845		0.67513	1.543	
67 1,4-Dinitrobenzene	+++++	+++++	+++++	+++++	+++++	0.16418			
	0.17086	0.17624	0.19193	+++++	0.18841		0.17832	6.559	
68 2,4,6-Trichlorophenol	+++++	+++++	+++++	+++++	0.38838	0.37875			
	0.36776	0.36632	0.35766	0.37602	0.38048		0.37362	2.763	
69 2,4,5-Trichlorophenol	+++++	+++++	+++++	+++++	0.43384	0.41372			
	0.40477	0.39028	0.38786	0.40586	0.39237		0.40410	4.007	
70 Meta-Dinitrobenzene	+++++	+++++	+++++	+++++	+++++	0.18184			
	0.19130	0.19875	0.20857	+++++	0.19232		0.19456	5.085	
71 1,3-Dinitrobenzene	+++++	+++++	+++++	+++++	+++++	0.18184			
	0.19130	0.19875	0.20857	+++++	0.19232		0.19456	5.085	

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	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
73 Isosafrole	+++++	+++++	+++++	+++++	0.48105	0.47477			
	0.48754	0.51275	0.50649	0.48096	0.47600		0.48851	3.093	
74 1,1'-Biphenyl	+++++	+++++	+++++	+++++	1.27869	1.25572			
	1.21795	1.21313	1.22313	1.15755	1.18277		1.21842	3.359	
75 2-Chloronaphthalene	+++++	+++++	+++++	+++++	1.01085	1.00903			
	0.98970	0.98072	1.00381	0.97597	0.98304		0.99330	1.449	
76 1-Chloronaphthalene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
77 3,4-Dichlorophenol	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
78 2-Nitroaniline	+++++	+++++	+++++	+++++	0.32630	0.34513			
	0.32711	0.27733	0.30181	0.28756	0.28485		0.30716	8.413	
79 1,4-Naphthoquinone	+++++	+++++	+++++	+++++	0.32442	0.32847			
	0.32489	0.32358	0.27146	0.21690	0.25291		0.29181	15.357	<-
80 Dimethylphthalate	+++++	+++++	+++++	+++++	1.16339	1.09588			
	1.11029	1.09953	1.10863	1.13722	1.07767		1.11323	2.560	
81 2,6-Dinitrotoluene	+++++	0.23642	0.25925	+++++	0.25862	0.25273			
	0.23891	0.24488	0.24961	0.27737	0.27582		0.25484	5.729	
82 2,3,5,6-Tetrachlorophenol	+++++	+++++	+++++	+++++	0.32678	0.33241			
	0.32743	0.34726	0.36535	0.34253	0.35417		0.34228	4.228	

INITIAL CALIBRATION DATA

Start Cal Date : 11-FEB-2005 15:50
End Cal Date : 11-OCT-2005 21:46
Quant Method : ISTD
Origin : Disabled
Target Version : 3.50
Integrator : HP RTE
Method file : /var/chem/gcl1.i/1011-8270-1.b/8270-1.m
Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	___ RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
83 o,o,o-TEPA	+++++	+++++	+++++	+++++	0.54763	0.50370			
	0.52723	0.62383	0.52747	0.48231	0.56187		0.53915	8.474	
84 Acenaphthylene	+++++	+++++	1.83712	+++++	1.67871	1.61834			
	1.55056	1.54598	1.53694	1.51656	1.52241		1.60083	6.886	
85 3-Nitroaniline	+++++	+++++	+++++	+++++	0.25928	0.27093			
	0.24453	0.23230	0.20340	0.20590	0.17501		0.22734	15.037	<-
87 Acenaphthene	+++++	+++++	1.17053	+++++	0.94039	0.93024			
	0.90892	0.90274	0.89443	0.91705	0.91472		0.94738	9.641	
88 2,4-Dinitrophenol	+++++	+++++	+++++	+++++	+++++	0.10209			
	0.12931	0.14963	0.12523	0.16676	0.15490		0.13799	17.076	<-
89 Diphenylamine	+++++	+++++	+++++	+++++	0.52167	0.49989			
	0.50219	0.56326	0.50979	+++++	0.49405		0.51514	4.935	
90 4-Nitrophenol	+++++	+++++	+++++	+++++	0.13233	0.16239			
	0.15971	0.11920	0.10468	0.16918	0.15868		0.14374	17.349	<-
91 Pentachlorobenzene	+++++	+++++	+++++	+++++	0.63186	0.62523			
	0.60410	0.60620	0.60341	0.60303	0.60153		0.61077	2.026	
92 Dibenzofuran	+++++	+++++	+++++	+++++	1.53735	1.51629			
	1.44722	1.42217	1.38770	1.43498	1.42681		1.45322	3.703	
93 2,4-Dinitrotoluene	+++++	+++++	+++++	+++++	0.34829	0.35334			
	0.34490	0.33602	0.31977	0.36314	0.31837		0.34055	4.938	

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Integrator : HP RTE
Method file : /var/chem/gcl1.i/1011-8270-1.b/8270-1.m
Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
94 bis(2-Ethylhexyl)adipate	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
95 1-Naphthylamine	+++++	+++++	+++++	+++++	1.10078	1.08766			
	0.97469	0.98642	1.14615	1.01417	1.09906		1.05842	6.238	
96 2-Naphthylamine	+++++	+++++	+++++	+++++	0.90128	0.85382			
	0.69360	0.75811	1.00734	0.87520	0.97066		0.86572	12.808	
97 Sym-Trinitrobenzene	+++++	+++++	+++++	+++++	+++++	0.12854			
	0.12348	0.12488	0.11468	+++++	0.12766		0.12385	4.456	
98 Diethylphthalate	+++++	+++++	+++++	+++++	1.18973	1.16794			
	1.13146	1.07996	1.11740	1.09474	1.05004		1.11875	4.383	
99 Fluorene	+++++	+++++	1.28491	+++++	1.21243	1.16568			
	1.11089	1.10075	1.08557	1.11768	1.09015		1.14601	6.166	
100 5-Nitro-o-Toluidine	+++++	+++++	+++++	+++++	+++++	0.12939			
	0.13451	0.14353	0.13989	0.13659	0.13188		0.13596	3.824	
101 4-Chlorophenyl-phenylether	+++++	+++++	+++++	+++++	0.58818	0.56738			
	0.53434	0.54262	0.54376	0.56327	0.53347		0.55329	3.669	
102 Diphenyl ether	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
103 4-Nitroaniline	+++++	+++++	+++++	+++++	0.25867	0.27566			
	0.25264	0.22898	0.20288	0.22651	0.21265		0.23686	11.091	

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Method file : /var/chem/gcl1.i/1011-8270-1.b/8270-1.m
Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
104 4,6-Dinitro-2-methylphenol	+++++	+++++	+++++	+++++	+++++	0.10392			
	0.11425	0.12328	0.12099	0.11590	0.11342		0.11529	5.889	
105 n-Nitrosodiphenylamine	+++++	+++++	0.51829	+++++	0.43028	0.41487			
	0.41789	0.40547	0.40372	0.40633	0.41033		0.42590	8.996	
106 1,2-Diphenylhydrazine	+++++	+++++	+++++	+++++	1.30563	1.39661			
	1.30165	1.24467	1.18674	1.13723	1.12286		1.24220	8.033	
108 Pentachloronitrobenzene	+++++	+++++	+++++	+++++	0.04129	0.04288			
	0.04383	0.04749	0.04317	+++++	0.03908		0.04296	6.519	
109 Phenacetin	+++++	+++++	+++++	+++++	0.27264	0.27001			
	0.27556	0.29083	0.24146	0.26127	0.24154		0.26476	6.862	
110 4-Bromophenyl-phenylether	+++++	+++++	+++++	+++++	0.22457	0.22874			
	0.23339	0.23226	0.23414	0.23658	0.23228		0.23171	1.698	
111 Diallate	+++++	+++++	+++++	+++++	0.25117	0.24442			
	0.24706	0.27000	0.23788	0.22752	0.20531		0.24048	8.413	
112 Hexachlorobenzene	+++++	0.30472	0.34929	+++++	0.29421	0.28826			
	0.28594	0.29196	0.29277	0.29463	0.29134		0.29924	6.511	
113 Simazine	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
114 Pentachlorophenol	+++++	+++++	+++++	+++++	+++++	0.12926			
	0.14390	0.16490	0.15907	0.17729	0.16679		0.15687	11.097	

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Method file : /var/chem/gc11.i/1011-8270-1.b/8270-1.m
Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
115 4-Aminobiphenyl	+++++	+++++	+++++	+++++	0.55917	0.54381			
	0.52225	0.60690	0.59860	0.58236	0.55383		0.56670	5.391	
116 Pronamide	+++++	+++++	+++++	+++++	0.29434	0.28189			
	0.27988	0.30101	0.28065	0.28098	0.27063		0.28419	3.566	
117 n-Octadecane	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
119 Phenanthrene	+++++	+++++	1.10894	+++++	0.95324	0.92266			
	0.95805	0.94821	0.92745	1.00189	0.98467		0.97564	6.154	
120 Anthracene	+++++	+++++	1.18531	+++++	1.02779	0.91555			
	0.98899	0.93566	0.90714	0.91762	0.89263		0.97134	10.062	
121 4-Nitroquinoline-1-Oxide	+++++	+++++	+++++	+++++	+++++	+++++			
	0.05094	0.06312	0.07008	+++++	0.06494		0.06227	13.018	
122 Carbazole	+++++	+++++	+++++	+++++	0.90187	0.89234			
	0.79575	0.80200	0.76372	0.80129	0.76466		0.81738	6.953	
123 Methapyrilene	+++++	+++++	+++++	+++++	+++++	0.19510			
	0.17245	0.15647	0.18650	+++++	0.14594		0.17129	11.901	
124 2,3,4,6-Tetrachlorophenol	+++++	+++++	+++++	+++++	0.34249	0.34831			
	0.35338	0.35671	0.36856	0.34886	0.33527		0.35051	3.030	
125 Di-n-butylphthalate	+++++	+++++	+++++	+++++	1.14649	1.13058			
	1.10005	1.09224	1.11288	1.06136	1.02090		1.09493	3.891	

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Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
126 5-Nitroacenaphthene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
127 Endothall	+++++	+++++	+++++	+++++	+++++	+++++			
	0.48736	0.78455	0.63373	0.57437	0.77492		0.65098	19.753	<-
128 Aramite	+++++	+++++	+++++	+++++	0.04515	0.04890			
	0.04893	0.05065	0.04970	+++++	0.04955		0.04882	3.903	
129 Isodrin	+++++	+++++	+++++	+++++	0.13556	0.13275			
	0.13662	0.14271	0.12796	+++++	0.11826		0.13231	6.360	
130 Fluoranthene	+++++	+++++	1.25890	+++++	1.15170	1.08977			
	1.03347	1.06407	1.00742	1.01348	0.97157		1.07380	8.679	
131 Benzidine	+++++	+++++	+++++	+++++	+++++	0.09011			
	0.06563	0.07643	0.07918	0.09180	0.09645		0.08327	13.879	
132 4,4MethyleneBis2Chloroaniline	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
133 Tris2,3DibromopropylPhosphate	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
134 Pyrene	+++++	+++++	1.35662	+++++	1.21202	1.20437			
	1.17436	1.22441	1.29297	1.30790	1.18692		1.24495	5.280	
135 2,3,7,8-TCDD	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-

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Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	___ RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
136 Kepone	+++++	+++++	+++++	+++++	0.06416	0.07077			
	0.07561	0.08765	0.09370	+++++	0.10450		0.08273	18.390	<-
138 Thionazin	+++++	+++++	+++++	+++++	0.45651	0.45552			
	0.45506	0.61020	0.48759	0.41855	0.56854		0.49314	14.145	
139 2-Sec-Butyl-4,6-Dinitrophenol	+++++	+++++	+++++	+++++	+++++	+++++			
	0.14818	0.16909	0.15676	0.16547	0.15920		0.15974	5.077	
140 P-Dimethylaminoazobenzene	+++++	+++++	+++++	+++++	+++++	0.23299			
	0.22901	0.24278	0.25044	0.23987	0.26219		0.24288	4.973	
141 Chlorobenzilate	+++++	+++++	+++++	+++++	0.35386	0.33994			
	0.34688	0.35874	0.35095	+++++	0.35752		0.35131	2.010	
142 3,3'-Dimethylbenzidine	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
143 Butylbenzylphthalate	+++++	+++++	+++++	+++++	0.49889	0.51417			
	0.51152	0.52118	0.53107	0.52537	0.50338		0.51508	2.258	
144 Sulfotep	+++++	+++++	+++++	+++++	0.38741	0.37478			
	0.39056	0.53402	0.43378	0.37413	0.51478		0.42992	15.765	<-
145 Phorate	+++++	+++++	+++++	+++++	1.70872	1.68355			
	1.64679	2.18669	1.79722	1.47262	1.98064		1.78232	13.208	
146 2-Acetylaminofluorene	+++++	+++++	+++++	+++++	+++++	0.42338			
	0.43343	0.47278	0.51323	+++++	0.54024		0.47661	10.544	

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Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
147 Dimethoate	+++++	+++++	+++++	+++++	0.98858	0.99935			
	0.97743	1.26658	1.09077	1.00862	1.16727		1.07123	10.260	
148 Carbofuran	+++++	+++++	+++++	+++++	1.23521	1.30057			
	1.31000	1.74792	1.44912	1.35079	1.62211		1.43082	13.190	
149 Benzyl benzoate	+++++	+++++	+++++	+++++	3.43673	3.19788			
	3.07492	3.85662	3.13256	2.54181	3.33297		3.22479	12.365	
150 3,3'-Dichlorobenzidine	+++++	0.31705	0.40353	+++++	0.39340	0.41059			
	0.39435	0.37829	0.36821	0.37822	0.37257		0.37958	7.237	
152 Benzo(a)anthracene	1.23633	1.10385	1.25273	+++++	1.19035	1.16560			
	1.12358	1.16650	1.12705	1.17908	1.13690		1.16820	4.156	
153 bis(2-Ethylhexyl)phthalate	+++++	+++++	+++++	+++++	0.72969	0.73197			
	0.73158	0.75106	0.74422	0.72375	0.70487		0.73102	2.025	
154 Chrysene	+++++	1.17781	1.27273	+++++	1.03365	1.03238			
	0.98484	1.04967	1.02745	0.99391	0.91746		1.05443	10.160	
155 Disulfoton	+++++	+++++	+++++	+++++	1.50535	1.43809			
	1.36607	1.71979	1.42036	1.14568	1.51837		1.44482	12.022	
156 6-Methylchrysene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
157 Methyl parathion	+++++	+++++	+++++	+++++	0.29374	0.32132			
	0.34346	0.47808	0.39871	0.39639	0.47562		0.38676	18.669	<-

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Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
158 Di-n-octylphthalate	+++++	+++++	+++++	+++++	1.30729	1.29977			
	1.22992	1.26952	1.26246	1.13759	1.09326		1.22854	6.702	
159 Malathion	+++++	+++++	+++++	+++++	0.92801	0.96102			
	0.93630	1.17982	0.97774	0.87807	1.07889		0.99141	10.431	
160 Parathion	+++++	+++++	+++++	+++++	0.03774	0.04028			
	0.04327	0.05563	0.04586	0.05373	0.05196		0.04692	14.827	
161 7,12-Dimethylbenz(a)anthracen	+++++	+++++	+++++	+++++	0.54755	0.52382			
	0.52752	0.57152	0.53870	+++++	0.49502		0.53402	4.795	
162 Benzo(j)fluoranthene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
163 Benzo(b)fluoranthene	1.49732	1.06174	1.17996	+++++	1.05554	1.27136			
	1.33535	1.19659	1.18581	+++++	+++++		1.22296	11.898	
164 Benzo(k)fluoranthene	1.35448	1.34839	1.46731	+++++	1.44791	1.17690			
	1.02898	1.16708	1.09320	+++++	+++++		1.26053	13.130	
165 Benzo(e)pyrene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
166 Benzo(a)pyrene	1.34450	1.11872	1.13221	+++++	1.05052	1.04420			
	1.00082	0.99328	0.99643	1.01625	1.00626		1.07032	10.124	
168 Perylene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-

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Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	___ RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
169 3-Methylcholanthrene	+++++	+++++	+++++	+++++	0.62335	0.58199			
	0.58685	0.63973	0.60639	+++++	0.54346		0.59696	5.707	
170 Famphur	+++++	+++++	+++++	+++++	1.47538	1.63385			
	1.64859	2.19676	1.81668	1.69245	1.74171		1.74363	12.959	
171 Diethylstilbestrol	+++++	+++++	+++++	+++++	0.42975	0.47913			
	0.52159	0.68259	0.57723	0.57937	0.59359		0.55189	15.041	<-
172 Dibenz(a,h)acridine	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
173 Dibenz(a,j)acridine	+++++	+++++	+++++	+++++	0.88832	0.86009			
	0.90890	0.97055	0.93382	+++++	0.84620		0.90131	5.160	
174 Indeno(1,2,3-cd)pyrene	1.78701	1.26551	1.37305	+++++	1.18570	1.23890			
	1.18986	1.10389	1.14700	1.18938	1.15966		1.26400	15.679	<-
175 Dibenzo(a,h)anthracene	1.32296	0.91404	1.09944	+++++	0.92523	0.94927			
	0.92114	0.87463	0.89247	0.95728	0.93912		0.97956	13.806	
176 Benzo(g,h,i)perylene	+++++	+++++	1.19681	+++++	1.00223	1.02500			
	0.98673	0.94151	0.97080	1.02522	1.01811		1.02080	7.526	
177 Hexachlorophene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
178 Dibenzo(a,e)pyrene	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-

INITIAL CALIBRATION DATA

Start Cal Date : 11-FEB-2005 15:50
End Cal Date : 11-OCT-2005 21:46
Quant Method : ISTD
Origin : Disabled
Target Version : 3.50
Integrator : HP RTE
Method file : /var/chem/gc11.i/1011-8270-1.b/8270-1.m
Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Compound	0.10000 Level 1	0.50000 Level 2	1.000 Level 3	2.000 Level 4	5.000 Level 5	10.000 Level 6	RRF	% RSD	
	20.000 Level 7	40.000 Level 8	50.000 Level 9	70.000 Level 10	80.000 Level 11				
241 Caprolactumm	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
242 Benzaldehyde	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
243 Atrazine	+++++	+++++	+++++	+++++	+++++	+++++			
	+++++	+++++	+++++	+++++	+++++		+++++	+++++	<-
$ 8 2-Fluorophenol	+++++	+++++	+++++	+++++	1.08185	1.09186			
	1.15229	1.11994	1.10792	1.16323	1.11877		1.11941	2.656	
$ 14 Phenol-d5	+++++	+++++	+++++	+++++	1.25942	1.32185			
	1.35027	1.21377	1.17486	1.21343	1.16947		1.24330	5.666	
$ 37 Nitrobenzene-d5	+++++	+++++	+++++	+++++	0.35173	0.36699			
	0.35156	0.34466	0.34678	0.34704	0.33679		0.34936	2.648	
$ 72 2-Fluorobiphenyl	+++++	+++++	+++++	+++++	1.14487	1.14727			
	1.10980	1.10013	1.14025	1.08209	1.08268		1.11530	2.574	
$ 107 2,4,6-Tribromophenol	+++++	+++++	+++++	+++++	0.29657	0.30506			
	0.28417	0.27789	0.26132	0.27936	0.27749		0.28312	5.020	
$ 137 Terphenyl-d14	+++++	+++++	+++++	+++++	0.76666	0.78494			
	0.77637	0.80482	0.85797	0.84005	0.78309		0.80199	4.302	

INITIAL CALIBRATION DATA

Start Cal Date : 11-FEB-2005 15:50
End Cal Date : 11-OCT-2005 21:46
Quant Method : ISTD
Origin : Disabled
Target Version : 3.50
Integrator : HP RTE
Method file : /var/chem/gcl1.i/1011-8270-1.b/8270-1.m
Cal Date : 20-Oct-2005 10:46 rynkarg
Curve Type : Average

Average %RSD Results.
Calculated Average %RSD = 8.95175743
Maximun Average %RSD = 15
* Passed Average %RSD Test.

Attachment 5.

Example: Acceptable Initial Calibration - Form 6

6B

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF1 =12i1102k.d RRF2 =12i1102j.d
RRF3 =12i1102i.d RRF4 =12i1102h.d RRF5 =12i1102g.d

COMPOUND	RRF1	RRF2	RRF3	RRF4	RRF5	RRF	% RSD
n-Nitrosodimethylamine					0.608		
4-Bromophenyl-phenylether					0.227		
Benzo(b)fluoranthene	1.706	1.690	1.767	1.855	1.895		
Di-n-octylphthalate							
Hexachlorobenzene		0.248	0.253	0.257	0.258		
Pentachlorophenol							
Chrysene		1.148	1.181	1.138	1.130		
Aniline							
bis(2-Ethylhexyl)phthalate					1.018		
Phenol					1.444		
bis(2-Chloroethyl)ether				1.098	1.213		
2-Chlorophenol					1.300		
1,3-Dichlorobenzene				1.478	1.508		
1,4-Dichlorobenzene				1.479	1.516		
1,2-Dichlorobenzene				1.429	1.458		
Benzyl alcohol							
2,2'-oxybis(1-Chloropropane				2.386	2.386		
2-Methylphenol				0.995	1.019		
o-Cresol				0.995	1.019		
N-Nitroso-di-n-propylamine #					0.804		#
Phenanthrene			1.108	1.091	1.100		
4-Methylphenol			0.995	1.041	1.051		
meta & para-Cresol			0.995	1.041	1.051		
Hexachloroethane					0.584		
Anthracene			1.086	1.104	1.141		
Nitrobenzene			0.497	0.497	0.504		
Carbazole					1.058		
Isophorone				0.494	0.507		
2-Nitrophenol							
2,4-Dimethylphenol							
bis(2-Chloroethoxy)methane				0.388	0.398		
2,4-Dichlorophenol							
Benzoic acid							
1,2,4-Trichlorobenzene				0.325	0.329		
Naphthalene			0.973	0.988	0.999		
Di-n-butylphthalate					1.464		
4-Chloroaniline							

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF1 =12i1102k.d RRF2 =12i1102j.d
RRF3 =12i1102i.d RRF4 =12i1102h.d RRF5 =12i1102g.d

COMPOUND	RRF1	RRF2	RRF3	RRF4	RRF5	RRF	% RSD
Hexachlorobutadiene					0.183		
Fluoranthene			1.185	1.191	1.222		
4-Chloro-3-methylphenol							
Benzidine							
2-Methylnaphthalene		0.829	0.849	0.856	0.894		
Hexachlorocyclopentadiene #							#
Pyrene			1.287	1.341	1.350		
2,4,6-Trichlorophenol					0.371		
2,4,5-Trichlorophenol					0.401		
Benzo(a)anthracene	1.487	1.187	1.172	1.218	1.256		
3,3'-Dichlorobenzidine					0.431		
2-Chloronaphthalene				1.304	1.275		
2-Nitroaniline					0.351		
Butylbenzylphthalate				0.665	0.691		
Dimethylphthalate				1.420	1.516		
Pyridine							
2,6-Dinitrotoluene		0.227	0.267	0.271	0.302		
Benzo(g,h,i)perylene			1.489	1.502	1.419		
Acenaphthylene			1.910	1.975	2.080		
3-Nitroaniline							
Acenaphthene			1.088	1.122	1.166		
2,4-Dinitrophenol #							#
Dibenzo(a,h)anthracene	1.557	1.285	1.512	1.522	1.507		
4-Nitrophenol #							#
Dibenzofuran				1.594	1.644		
2,4-Dinitrotoluene			0.313	0.352	0.390		
Indeno(1,2,3-cd)pyrene	1.867	1.137	1.756	1.419	1.430		
Diethylphthalate				1.528	1.561		
Fluorene			1.336	1.368	1.395		
4-Chlorophenyl-phenylether					0.668		
4-Nitroaniline							
4,6-Dinitro-2-methylphenol							
n-Nitrosodiphenylamine (1)			0.608	0.613	0.637		
1,2-Diphenylhydrazine					1.432		
Benzo(a)pyrene	1.558	1.462	1.464	1.541	1.596		

(1) Cannot be separated from Diphenylamine

6C

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF1 =12i1102k.d RRF2 =12i1102j.d
RRF3 =12i1102i.d RRF4 =12i1102h.d RRF5 =12i1102g.d

COMPOUND	RRF1	RRF2	RRF3	RRF4	RRF5	RRF	% RSD
Benzo(k)fluoranthene	1.704	1.864	1.669	1.706	1.780		
2-Picoline				1.124	1.202		
n-Nitrosomethylethylamine					0.530		
Methyl Methanesulfonate				0.429	0.456		
n-Nitrosodiethylamine				0.650	0.665		
Ethyl Methanesulfonate				0.815	0.823		
o-Toluidine				1.397	1.414		
n-Nitrosopiperidine				0.225	0.245		
2,6-Dichlorophenol				0.262	0.279		
Hexachloropropene				0.199	0.205		
n-Nitrosodi-N-Butylamine				0.197	0.219		
Safrole				0.219	0.225		
1,2,4,5-Tetrachlorobenzene				0.617	0.624		
Isosafrole					0.521		
1,4-Naphthoquinone					0.260		
Pentachlorobenzene				0.537	0.573		
1-Naphthylamine				0.804	0.841		
2-Naphthylamine				0.257	0.199		
Diallate					0.426		
Phenacetin					0.332		
5-Nitro-o-Toluidine							
4-Aminobiphenyl					0.254		
Pronamide				0.296	0.310		
Chlorobenzilate				0.405	0.413		
P-Dimethylaminoazobenzene							
3,3'-Dimethylbenzidine							
2-Acetylaminofluorene					0.496		
3-Methylcholanthrene				0.753	0.743		
Isodrin				0.207	0.220		
Pentachloroethane				0.527	0.529		
2-Fluorophenol			1.062	1.093	1.115		
Terphenyl-d14				0.824	0.845		
2-Fluorobiphenyl				1.292	1.337		
Nitrobenzene-d5				0.309	0.319		

6C

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF1 =12i1102k.d RRF2 =12i1102j.d
RRF3 =12i1102i.d RRF4 =12i1102h.d RRF5 =12i1102g.d

COMPOUND	RRF1	RRF2	RRF3	RRF4	RRF5	RRF	% RSD
Phenol-d5			1.316	1.336	1.382		
2,4,6-Tribromophenol			0.207	0.221	0.228		

6B

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF6 =12i1102f.d RRF7 =12i1102e.d
RRF8 =12i1102d.d RRF9 =12i1102c.d RRF10 =12i1102b.d

COMPOUND	RRF6	RRF7	RRF8	RRF9	RRF10	RRF	% RSD
n-Nitrosodimethylamine	0.569	0.667	0.659	0.432	0.546		
4-Bromophenyl-phenylether	0.224	0.227	0.225	0.231	0.229		
Benzo(b)fluoranthene	1.904	1.840	2.085	1.899	1.911		
Di-n-octylphthalate	2.829	2.675	2.372	2.634	2.473		
Hexachlorobenzene	0.259	0.258	0.248	0.246	0.260		
Pentachlorophenol	0.104	0.111	0.120	0.124	0.138		
Chrysene	1.136	1.085	1.007	1.116	1.050		
Aniline	1.283	1.382	1.402	1.417	1.505		
bis(2-Ethylhexyl)phthalate	1.041	0.976	0.901	0.989	0.931		
Phenol	1.426	1.382	1.308	1.412	1.426		
bis(2-Chloroethyl)ether	1.201	1.166	1.150	1.136	1.107		
2-Chlorophenol	1.266	1.231	1.205	1.218	1.216		
1,3-Dichlorobenzene	1.470	1.434	1.392	1.420	1.404		
1,4-Dichlorobenzene	1.500	1.457	1.411	1.451	1.432		
1,2-Dichlorobenzene	1.414	1.413	1.389	1.401	1.386		
Benzyl alcohol	0.672	0.714	0.706	0.780	0.745		
2,2'-oxybis(1-Chloropropane	2.375	2.337	2.289	2.289	2.279		
2-Methylphenol	1.032	1.010	1.001	1.071	1.079		
o-Cresol	1.032	1.010	1.001	1.071	1.079		
N-Nitroso-di-n-propylamine #	0.810	0.794	0.538	0.872	0.816		#
Phenanthrene	1.086	1.117	1.100	1.023	1.108		
4-Methylphenol	1.056	1.037	1.005	1.112	1.079		
meta & para-Cresol	1.056	1.037	1.005	1.112	1.079		
Hexachloroethane	0.573	0.563	0.533	0.544	0.517		
Anthracene	1.143	1.113	1.009	1.077	1.061		
Nitrobenzene	0.493	0.483	0.472	0.476	0.467		
Carbazole	1.059	1.083	1.003	1.030	1.020		
Isophorone	0.524	0.536	0.420	0.578	0.560		
2-Nitrophenol	0.176	0.184	0.189	0.185	0.188		
2,4-Dimethylphenol	0.319	0.321	0.320	0.337	0.325		
bis(2-Chloroethoxy)methane	0.403	0.400	0.404	0.397	0.404		
2,4-Dichlorophenol	0.282	0.286	0.285	0.296	0.286		
Benzoic acid	0.158	0.197	0.210	0.205	0.195		
1,2,4-Trichlorobenzene	0.326	0.324	0.314	0.308	0.297		
Naphthalene	0.986	0.977	0.956	0.946	0.930		
Di-n-butylphthalate	1.472	1.432	1.280	1.365	1.251		
4-Chloroaniline	0.311	0.343	0.338	0.328	0.331		

6C

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF6 =12i1102f.d RRF7 =12i1102e.d
RRF8 =12i1102d.d RRF9 =12i1102c.d RRF10 =12i1102b.d

COMPOUND	RRF6	RRF7	RRF8	RRF9	RRF10	RRF	% RSD
Hexachlorobutadiene	0.182	0.177	0.175	0.170	0.166		
Fluoranthene	1.215	1.202	1.109	1.115	1.116		
4-Chloro-3-methylphenol	0.276	0.274	0.270	0.287	0.272		
Benzidine	0.214	0.306	0.418	0.325	0.410		
2-Methylnaphthalene	0.901	0.876	0.861	0.888	0.856		
Hexachlorocyclopentadiene #		0.385	0.398	0.376	0.398		#
Pyrene	1.373	1.313	1.252	1.414	1.291		
2,4,6-Trichlorophenol	0.374	0.371	0.372	0.371	0.373		
2,4,5-Trichlorophenol	0.402	0.395	0.394	0.401	0.392		
Benzo(a)anthracene	1.286	1.258	1.276	1.231	1.244		
3,3'-Dichlorobenzidine	0.424	0.435	0.431	0.412	0.421		
2-Chloronaphthalene	1.276	1.110	0.840	1.147	1.088		
2-Nitroaniline	0.359	0.362	0.363	0.356	0.349		
Butylbenzylphthalate	0.710	0.675	0.643	0.697	0.659		
Dimethylphthalate	1.548	1.495	1.462	1.452	1.394		
Pyridine	0.885	1.162	1.199	0.759	0.928		
2,6-Dinitrotoluene	0.306	0.293	0.271	0.270	0.279		
Benzo(g,h,i)perylene	1.381	1.477	1.460	1.581	1.459		
Acenaphthylene	2.007	1.931	1.872	1.832	1.798		
3-Nitroaniline	0.303	0.303	0.307	0.284	0.290		
Acenaphthene	1.145	1.113	1.074	1.086	1.056		
2,4-Dinitrophenol #		0.134	0.162	0.145	0.150		#
Dibenzo(a,h)anthracene	1.424	1.468	1.457	1.529	1.464		
4-Nitrophenol #		0.160	0.158	0.154	0.155		#
Dibenzofuran	1.636	1.557	1.514	1.502	1.462		
2,4-Dinitrotoluene	0.406	0.396	0.387	0.380	0.370		
Indeno(1,2,3-cd)pyrene	1.410	1.588	1.628	1.625	1.810		
Diethylphthalate	1.561	1.468	1.365	1.408	1.294		
Fluorene	1.381	1.319	1.254	1.243	1.203		
4-Chlorophenyl-phenylether	0.663	0.628	0.599	0.598	0.588		
4-Nitroaniline	0.302	0.282	0.304	0.285	0.290		
4,6-Dinitro-2-methylphenol	0.103	0.118	0.100	0.122	0.127		
n-Nitrosodiphenylamine (1)	0.633	0.619	0.590	0.615	0.604		
1,2-Diphenylhydrazine	1.419	1.346	1.288	1.279	1.222		
Benzo(a)pyrene	1.581	1.572	1.545	1.568	1.553		

(1) Cannot be separated from Diphenylamine

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF6 =12i1102f.d RRF7 =12i1102e.d
RRF8 =12i1102d.d RRF9 =12i1102c.d RRF10 =12i1102b.d

COMPOUND	RRF6	RRF7	RRF8	RRF9	RRF10	RRF	% RSD
Benzo(k)fluoranthene	1.814	1.764	1.336	1.638	1.561		
2-Picoline	1.110	1.306	1.304	1.003			
n-Nitrosomethylethylamine	0.748	0.757	0.779	0.762	0.764		
Methyl Methanesulfonate	0.448	0.459	0.468	0.458	0.470		
n-Nitrosodiethylamine	0.643	0.651	0.646	0.648	0.590		
Ethyl Methanesulfonate	0.814	0.834	0.820	0.858	0.884		
o-Toluidine	1.427	1.461	1.452	1.540	1.504		
n-Nitrosopiperidine	0.251	0.255	0.263	0.271	0.266		
2,6-Dichlorophenol	0.283	0.278	0.277	0.286	0.276		
Hexachloropropene	0.204	0.212	0.219	0.204	0.207		
n-Nitrosodi-N-Butylamine	0.224	0.232	0.230	0.249	0.237		
Safrole	0.231	0.232	0.235	0.238	0.233		
1,2,4,5-Tetrachlorobenzene	0.599	0.582	0.573	0.563	0.569		
Isosafrole	0.520	0.622	0.778	0.521	0.666		
1,4-Naphthoquinone	0.276	0.274	0.266	0.268	0.265		
Pentachlorobenzene	0.553	0.539	0.525	0.530	0.516		
1-Naphthylamine	0.623	0.617	0.790	0.455	0.694		
2-Naphthylamine	0.125	0.206	0.377	0.168	0.328		
Diallate	0.405	0.361	0.257	0.276	0.268		
Phenacetin	0.324	0.318	0.307	0.317	0.316		
5-Nitro-o-Toluidine	0.152	0.144	0.127	0.154	0.160		
4-Aminobiphenyl	0.211	0.352	0.428	0.302	0.416		
Pronamide	0.318	0.310	0.295	0.309	0.309		
Chlorobenzilate	0.425	0.405	0.392	0.454	0.411		
P-Dimethylaminoazobenzene	0.344	0.332	0.324	0.347	0.329		
3,3'-Dimethylbenzidine	0.475	0.490	0.464	0.392	0.417		
2-Acetylaminofluorene	0.473	0.525	0.548	0.509	0.540		
3-Methylcholanthrene	0.730	0.772	0.771	0.796	0.776		
Isodrin	0.214	0.204	0.186	0.233	0.205		
Pentachloroethane	0.536	0.521	0.514	0.525	0.520		
2-Fluorophenol	1.115	1.117	1.113	1.093	1.114		
Terphenyl-d14	0.871	0.830	0.818	0.915	0.848		
2-Fluorobiphenyl	1.282	1.268	1.242	1.242	1.239		
Nitrobenzene-d5	0.314	0.320	0.310	0.306	0.300		

6C

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF6 =12i1102f.d RRF7 =12i1102e.d
RRF8 =12i1102d.d RRF9 =12i1102c.d RRF10 =12i1102b.d

COMPOUND	RRF6	RRF7	RRF8	RRF9	RRF10	RRF	% RSD
Phenol-d5	1.359	1.333	1.267	1.354	1.362		
2,4,6-Tribromophenol	0.225	0.233	0.234	0.215	0.218		

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF11 =12i1102a.d RRF12 =12i0611a.d

COMPOUND	RRF11	RRF12				RRF	% RSD
n-Nitrosodimethylamine						0.580	15.0
4-Bromophenyl-phenylether	0.232					0.228	1.4
Benzo(b)fluoranthene	1.936					1.862	6.0
Di-n-octylphthalate						2.597	6.9
Hexachlorobenzene	0.252					0.254	2.0
Pentachlorophenol	0.125					0.120	9.8
Chrysene	1.091					1.108	4.6
Aniline	1.697					1.448	9.8
bis(2-Ethylhexyl)phthalate	0.969					0.975	4.9
Phenol	1.602					1.428	6.2
bis(2-Chloroethyl)ether	1.206					1.160	3.9
2-Chlorophenol	1.304					1.248	3.3
1,3-Dichlorobenzene	1.448					1.444	2.7
1,4-Dichlorobenzene	1.496					1.468	2.5
1,2-Dichlorobenzene	1.451					1.418	1.9
Benzyl alcohol	0.902					0.753	10.8
2,2'-oxybis(1-Chloropropane	2.441					2.348	2.5
2-Methylphenol	1.223					1.054	7.1
o-Cresol	1.223					1.054	7.1
N-Nitroso-di-n-propylamine #	0.930					0.795	15.5#<-
Phenanthrene	0.997					1.081	3.9
4-Methylphenol	1.226					1.067	6.5
meta & para-Cresol	1.226					1.067	6.5
Hexachloroethane	0.534					0.550	4.4
Anthracene	1.038					1.086	4.1
Nitrobenzene	0.478					0.485	2.7
Carbazole	0.977					1.033	3.5
Isophorone	0.588					0.526	10.3
2-Nitrophenol	0.192					0.186	3.0
2,4-Dimethylphenol	0.336					0.326	2.5
bis(2-Chloroethoxy)methane	0.410					0.400	1.6
2,4-Dichlorophenol	0.297					0.289	2.2
Benzoic acid	0.194					0.193	9.5
1,2,4-Trichlorobenzene	0.297					0.315	4.1
Naphthalene	0.935					0.966	2.6
Di-n-butylphthalate	1.228					1.356	7.6
4-Chloroaniline	0.330					0.330	3.3

6C

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF11 =I2106102a.d RRF12 =I2106111a.d

COMPOUND	RRF11	RRF12				RRF	% RSD	
Hexachlorobutadiene	0.163					0.174	4.4	
Fluoranthene	1.046					1.156	5.3	
4-Chloro-3-methylphenol	0.282					0.277	2.3	
Benzidine	0.337					0.335	22.4	<-
2-Methylnaphthalene	0.884					0.869	2.6	
Hexachlorocyclopentadiene #	0.415					0.394	3.8	#
Pyrene	1.459					1.342	4.9	
2,4,6-Trichlorophenol	0.386					0.374	1.5	
2,4,5-Trichlorophenol	0.399					0.398	1.0	
Benzo(a)anthracene	1.241					1.260	6.6	
3,3'-Dichlorobenzidine	0.401					0.422	2.8	
2-Chloronaphthalene	1.093					1.142	13.2	
2-Nitroaniline	0.347					0.355	1.8	
Butylbenzylphthalate	0.699					0.680	3.4	
Dimethylphthalate	1.454					1.468	3.4	
Pyridine						0.987	19.1	<-
2,6-Dinitrotoluene	0.253					0.274	8.5	
Benzo(g,h,i)perylene	1.532					1.478	4.0	
Acenaphthylene	1.822					1.914	4.9	
3-Nitroaniline	0.285					0.295	3.4	
Acenaphthene	1.077					1.103	3.3	
2,4-Dinitrophenol #	0.141					0.146	7.0	#
Dibenzo(a,h)anthracene	1.532					1.478	5.1	
4-Nitrophenol #	0.152					0.156	1.9	#
Dibenzofuran	1.501					1.551	4.4	
2,4-Dinitrotoluene	0.372					0.374	7.4	
Indeno(1,2,3-cd)pyrene	1.603					1.570	13.4	
Diethylphthalate	1.331					1.440	7.3	
Fluorene	1.198					1.300	5.9	
4-Chlorophenyl-phenylether	0.592					0.619	5.5	
4-Nitroaniline	0.289					0.292	3.2	
4,6-Dinitro-2-methylphenol	0.124					0.116	10.0	
n-Nitrosodiphenylamine (1)	0.599					0.613	2.5	
1,2-Diphenylhydrazine	1.236					1.317	6.4	
Benzo(a)pyrene	1.608					1.550	3.1	

(1) Cannot be separated from Diphenylamine

6C

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF11 =I2i1102a.d RRF12 =I2i0611a.d

COMPOUND	RRF11	RRF12				RRF	% RSD	
Benzo(k)fluoranthene	1.639					1.680	8.5	
2-Picoline						1.175	10.1	
n-Nitrosomethylethylamine	0.736					0.725	12.0	
Methyl Methanesulfonate	0.502					0.461	4.5	
n-Nitrosodiethylamine	0.717					0.651	5.3	
Ethyl Methanesulfonate	0.990					0.855	7.0	
o-Toluidine	1.734					1.491	7.3	
n-Nitrosopiperidine	0.276					0.256	6.4	
2,6-Dichlorophenol	0.287					0.278	2.8	
Hexachloropropene	0.202					0.206	3.1	
n-Nitrosodi-N-Butylamine	0.247					0.229	7.2	
Safrole	0.242					0.232	3.0	
1,2,4,5-Tetrachlorobenzene	0.592					0.590	3.8	
Isosafrole	0.586					0.602	16.0	<-
1,4-Naphthoquinone	0.269					0.268	2.0	
Pentachlorobenzene	0.530					0.538	3.3	
1-Naphthylamine	0.590					0.677	19.3	<-
2-Naphthylamine	0.271					0.241	34.7	<-
Diallate	0.246					0.320	23.6	<-
Phenacetin	0.311					0.318	2.5	
5-Nitro-o-Toluidine	0.165					0.150	8.9	
4-Aminobiphenyl	0.378					0.334	24.5	<-
Pronamide	0.304					0.306	2.5	
Chlorobenzilate	0.461					0.421	5.8	
P-Dimethylaminoazobenzene	0.349					0.338	3.1	
3,3'-Dimethylbenzidine	0.350					0.431	12.6	
2-Acetylaminofluorene						0.515	5.5	
3-Methylcholanthrene	0.801					0.768	3.2	
Isodrin	0.251					0.215	9.2	
Pentachloroethane	0.536					0.526	1.5	
2-Fluorophenol	1.148					1.108	2.1	
Terphenyl-d14	0.947					0.862	5.4	
2-Fluorobiphenyl	1.300					1.275	2.7	
Nitrobenzene-d5	0.302					0.310	2.4	

6C

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: STL-CHICAGO Contract:

Lab Code: Case No.: SAS No.: SDG No.: 1102-8270-12

Instrument ID: GCL12 Calibration Date(s): 06/11/04 11/02/04

Min RRF for SPCC(#) = 0.050 Max %RSD for CCC(*) = 30.0%

LAB FILE ID: RRF11 =I2i1102a.d RRF12 =I2i0611a.d

COMPOUND	RRF11	RRF12				RRF	% RSD
Phenol-d5	1.543					1.361	5.6
2,4,6-Tribromophenol	0.214					0.222	4.1

Attachment 6.

GC/MS Calibration - Evaluation and Acceptance Criteria

GCMS Calibration – Evaluation and Acceptance Criteria

Prepare standards	• The concentrations must cover the range of quantitation for all analytes • The lowest point of the calibration curve must be at, or below, the reporting limit	
Run calibration standards	• All analytes must contain at a minimum 5 calibration points for Linear regressions, linear curves, or average response factors • Analytes using second order fits must have a minimum of 6 calibration points on a curve • Analytes using 3rd order curves must have a minimum of 7 calibration points	• Calibration levels deemed to be statistical or visual outliers shall be dropped from the curve and replaced by a similar concentration standard. The standard shall be dropped in its entirety, not on a per analyte basis
Calculate "grand mean RSD" of all compounds	• The "grand mean RSD" is calculated before attempting to fit compounds to any calibration curves only because it is easier to do at this time. The "grand mean RSD" acceptance is only to be used as a last resort in determining whether a compound's calibration is acceptable. • Calibrations for compounds which occur on different dates (i.e appix compounds analyzed at different dates than the HSL compounds), the "grand mean RSD" is calculated separately for each curve.	• If no %RSD for any given compound is above 15%, the "grand mean RSD will be less than 15%.
Evaluation each compound for linear fit, second order fit or 3rd order fit	• Having determined that the calibration meets minimum requirements, the laboratory will evaluate each compound to determine the best calibration fit using statistical and visual evaluation of the curve • Using "priori" knowledge some compounds ranges may be shortened (i.e. not as low a reporting limit or not as high a range)	• Citing priori knowledge the laboratory may decide to "keep" calibrations for several compounds despite exceeding the statistical threshold allowed by the method. The compounds that fall in this category are known poor performers as indicated by the method or as indicated from historical performance data (e g: Appendix IX compounds) These compounds will be listed in the QP as possible trouble analytes. Quantitation for these compounds may be biased and should be used only with caution.
Determine the best calibration approach for each compound	• RRF • Linear • 2nd order • Grand Mean RSD	• Even when the "grand mean RSD" indicates minimum acceptance has been met, the analyst must use discretion for quantification because some compounds may be biased This approach must be used with caution.

Attachment 7.

Example: Semi-Volatile Analysis Logbook

STL Chicago
GC/MS Semi-Volatiles Analysis Logbook

Instrument ID# 01

CHI-22-21-002/K-03/05

Analysis Date/ Time	File Name	Sample Number	Client / Sample ID	Sample Prep.	Instr Dil.	Int. Std. No.	Final Vol. (mL)	Comments	Need Re-anal-ysis	Need Dil.	Analyst Initial

Analyst Signature: _____ Date_____ Reviewer Signature: _____ Date_____ Page No._____

Attachment 8.

Example: Sample Corrective Action Report

STL Chicago

Instrument ID # 01 **GC/MS Semi-Volatiles Corrective Action / Qualification Report** Page No._____

Tune Name:_____ **Performance of daily maintenance by:** Analyst Initials _____Date_____

Methods: __SW846 8270C __SW846 8270SIM __ USEPA OLM04.2 __USEPA OLC02.1 __ 40CFR 625 _Other_____

Tune Criteria

Description of Situation:_____

Action Taken:_____

Demonstration of Control:_____

Initial Calibration Cirteria

Description of Situation:_____

Action Taken:_____

Demonstration of Control_____

Continuing Calibration Criteria

Description of Situation:_____

Action Taken:_____

Demonstration of Control:_____

Internal Standards (continuing cal to continuing cal)

Description of Situation:_____

Action Taken:_____

Demonstration of Control:_____

Qualification of Data

Data Affected (Client/Sample #)_____

Qualification:_____

Associated samples reanalyzed: Yes No (see below)

Explanation for no reanalysis/data MUST be qualified and narrated:_____

Analyst Signature _____Date_____

Reviewer Signature _____Date_____

Attachment 9.

Example: Data Review Checklist

STL Chicago

GCMS DATA REVIEW CHECKLIST

Site Name:_____ Primary Reviewer:_____ Review Date:_____

JOB Number: _____ Secondary Reviewer:_____ Review Date:_____

No. of Samples/Matrix: a)_____ WATER b)_____ SOIL c)_____ SPLP / TCLP d)_____ Other (_____)

Method: a) VOA _____ 5030_____ Encores: 5035--High _____ 5035-Low_____ b) BNA _____

Report Type: a) MDL U b) RL U c) ND d) Breach e) P1 / P2 (Printed QC must match PM selected Report Type)

TASK	PRI REV	SEC REV	COMMENTS
LAB CHRON: 1) Matches Big Board (Job Analysis History)			
2) Matches Raw Data (Form 4 / 5)			
3) Note Sample dilutions and list reason. a) High Sample Conc. b) Interference present IF **original** and **re-run** are to be reported in LabNet Re-log Samples (Indicate data type used) Re-Analyzed (RE) Re-Extracted (RA) Dilution (DL)			Smp # Original Dilution Comments BNA Only: Final Volume Adjustment _____
4) Sample Hold Times Met			
5) Proper Prep Links Created S-F6: Routine Preps; 5035PL; 5035PH S-F9: TCLP; SPLP ; 5035 Archon Purge & Trap			
Incomplete JOB Status Report reveals No Outstanding Data			
PROJ. REQ. MET: 1) Sample Detection Limit Met			
2) Reported J values meet reporting criteria			
3) Method Blank Detection Limits Met			
4) Project Specific Compounds of Concern : Yes No			
LabNet Report matches Quant Report: Sample weights / Volumes / % Moisture / Factors verified			
Manual Integration documentation / verification complete			
FORM 2: Surrogate Recoveries Within Limits Statistical Limits _____ Method Limits _____ Project Limits _____(S-F10 used to Clone By Project) AFCEE___; LCG___; QAPP___ Directed Note to PM: Yes / No			Smp # Original Re-analysis Comments
FORM 3: MS/MSD Recoveries Acceptable Statistical Limits _____ Method Limits _____ Project Limits _____(S-F10 used to Clone By Project) AFCEE___; LCG___; QAPP___ Directed Note to PM: Yes / No			Smp # _____ MS MSD RPD
FORM 3: LCS Recoveries Acceptable (LCD if no MS/MSD) Statistical Limits _____ Method Limits _____ Project Limits _____(S-F10 used to Clone By Project) AFCEE___; LCG___; QAPP___ Directed Note to PM: Yes / No			Batch # _____ Batch # _____ Batch # _____ Batch # _____ Batch # _____ Batch # _____

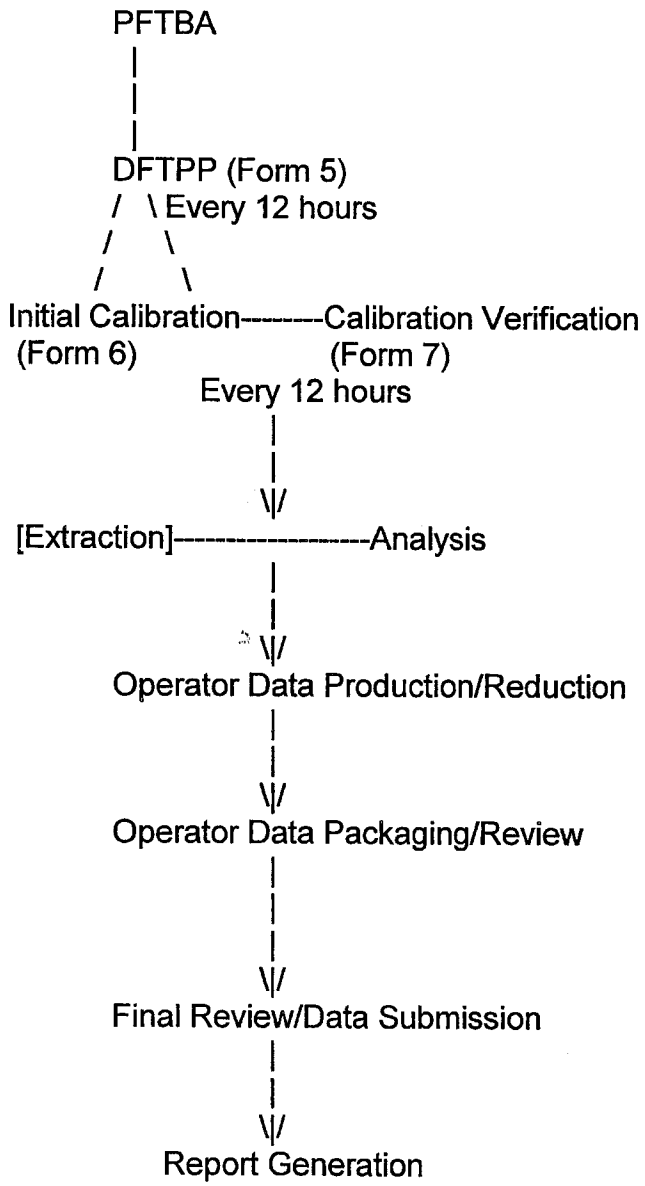
TASK	PRI REV	SEC REV	COMMENTS
FORM 5: Tuning Criteria Met			
FORM 6: Initial Calibration Criteria Met			
ICAL Spike Required: Yes No Control Limit applied: _____			
FORM 7: Daily Calibration (CCV) Criteria Met			
MRL Check Required: Yes No (LCG Requirement – Before and after Sample analysis) Control Limit Applied: _____			Before: After: Batch # _____ Batch # _____ Batch # _____ Batch # _____ Batch # _____
FORM 8: Internal Standards Criteria Met Directed Note to PM: Yes / No			Smp # Original Re-analysis Comments
LabNet Batch Status Report Displays Data at RPT / RVWD Status	RPT	RVWD	
RAW DATA: 1) Raw Data Verified/Complete			
2) Raw Data Matches Forms			
3) 5035 Prep Log page present / verified			
4) Quant Report Matches Spectra			
5) Manual integration reports (befores and afters) present (when required by client) and reason correctly documented and approved. Manual Integration Summary Printed: Yes No			File ID:
NARRATIVE: 1) Holding Times			
2) Method References			
3) % Recoveries / RPD's			
4) Analytical Difficulties/Typos/CAR's Directed Note to PM: Yes / No			
Manual Calculation of On Column result: Response Factor (Smp) x Concentration of IS IS Response Factor (Smp) Cmpd. RRF (Cont.Calib)			Sample : _____ Compound: _____

Additional Comments:

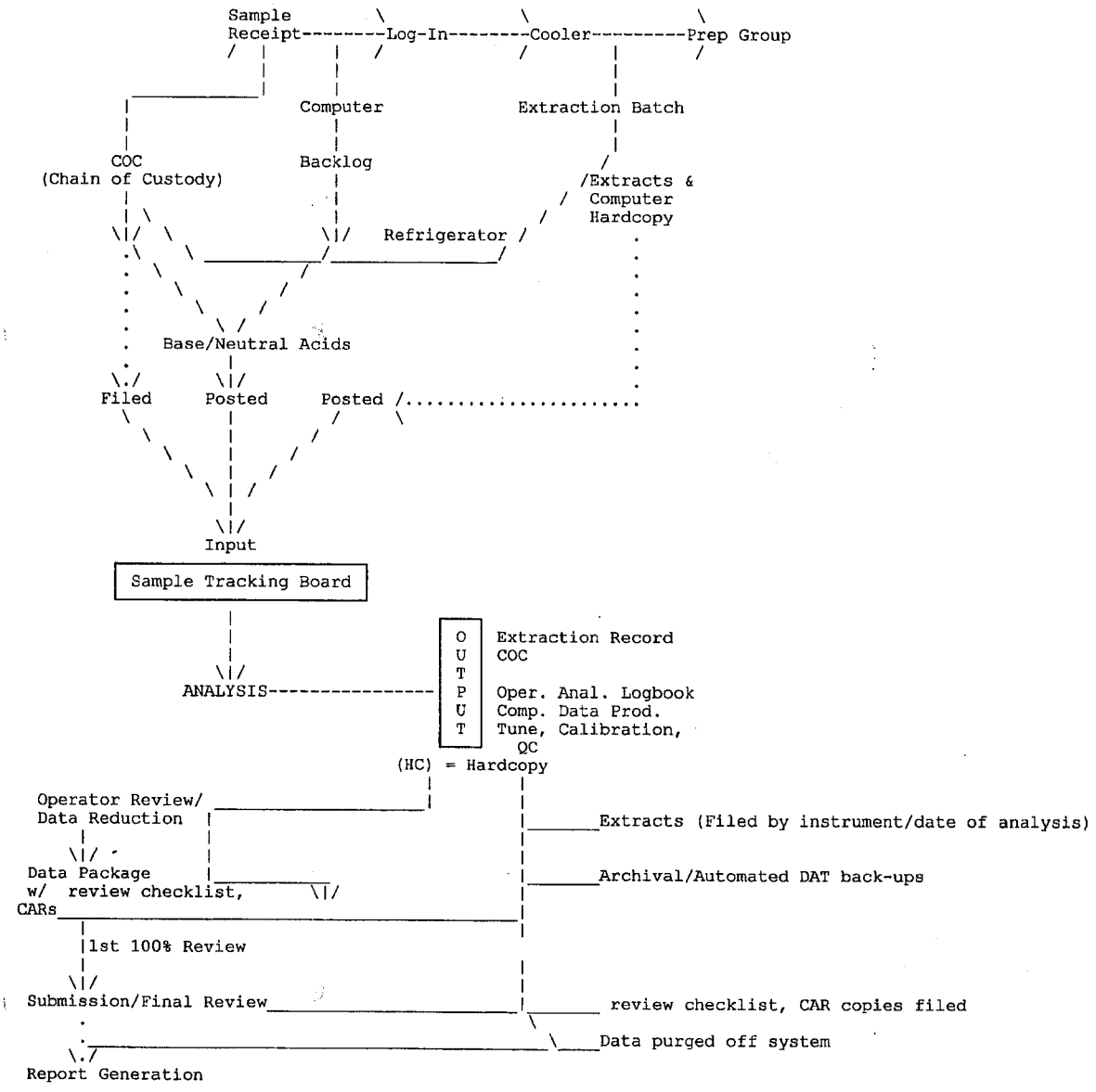
Attachment 10.

Analysis Scheme Flowchart

(Terms defined in the Section 6)



Sample Tracking Flowchart (for EACH unique STL batch #)



Attachment 11.

STL Corporate SOP, S-Q-004, 'Acceptable Manual Integration Practices and example documentation

Approvals and Signatures

Senior Vice President & Chief Operating Officer:	Dr. Keith C. Wheatstone	Date: 9/20/2004
Vice President, Client and Operations Services:	Dr. Charles W. Carter	Date: 9/20/2004
Corporate Quality Director:	Raymond J. Frederici	Date: 9/20/2004

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1.0 PURPOSE

This document describes STL's policy for proper manual peak integrations and requirements for documentation and review of manual peak integrations performed during the course of analyses.

2.0 SCOPE

This policy shall be enforced and followed throughout the laboratory. It applies to all STL laboratories for any analytical procedure involving identification or quantitation based on peak

analysis (e.g., GC, GC/MS, HPLC, IC). Each laboratory may have supplemental manual integration procedures or an addendum to this policy that describes additional details necessary to implement and enforce this policy. Any supplemental procedure or addendum must adhere to the requirements set forth in this policy.

3.0 POLICY

3.1 Supervisors must ensure proper training to all analysts and data reviewers using peak integration techniques. Analysts and data reviewers using peak integration techniques must be familiar with this policy and the applicable data processing system. This is to ensure that integration parameters are used in a manner that minimizes the need for manual integrations and that circumstances requiring manual integrations are performed in accordance with acceptable practices, documented and reviewed by a peer or supervisor. Audit trails or tracking systems MUST BE activated when the chromatographic system has this feature.

3.2 In some situations, manual integrations are necessary to compensate for imperfect chromatography, but manual integration must be performed ONLY when necessary. Baseline upsets, coelution and peak shape variation can sometimes complicate automatic integration and analyst intervention through manual integration may be required to assure consistency between area assignment for standards and samples.

3.3 Proper consistent manual integration is a critical quality control requirement. Appropriate manual integration is integration that can be technically justified. Manual integrations shall not be used to manipulate analytical results in order to meet method- or project-specific quality control (QC) acceptance criteria. Integration below the baseline is never appropriate. Inappropriate and inconsistent chromatographic peak integration to meet quality requirements is never allowed, nor is it to be used as a substitute for corrective action on the chromatographic system. Willful failure to follow this policy shall result in disciplinary action, up to and including termination.

3.4 The same integration technique must be applied **consistently** to any chromatogram i.e., field samples, calibration standards, calibration verification standards, and other applicable QC, etc., within the same analytical batch affected by the manual integration. Consistency in integration between standards and samples is one of the most important considerations in quantitative chromatographic analysis. Examples of appropriate and improper integration can be found in Appendix I and II.

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4.0 REASONS TO MANUALLY INTEGRATE

4.1 Undetected Peak

Routine mass spectrometer instrument tuning or the analysis of highly contaminated samples sometimes causes the relative abundances of ions of compounds present to deviate from reference criteria causing a peak to go undetected by the data system. A slight shift in chromatographic retention times can result in undetected peaks or false positive identification of compounds. If sample surrogate(s) retention times (RTs) shift, sample peaks need to be reviewed to ensure proper peak identification.

4.2 Incorrect Peak Integration

- Peak has small amount of splitting and the whole peak area was not integrated.
- Peaks close in retention times utilizing the same quantitation ions often integrate together as one peak, for example: ethylbenzene, xylenes; dichlorobenzenes, benzo(b)fluoranthene and benzo(k)fluoranthene.

4.3 Baseline Correction

- Matrix interferences caused by contaminated samples may interfere with calibrated compounds.

4.4 Other Examples of Events Requiring Manual Integration

- Incorrectly identified peak, where the wrong peak is chosen by the data system. This can occur both with the primary and the secondary ions.
- To remove a shoulder from a peak or to integrate a peak that only appears as a shoulder.

5.1 DATA SYSTEM PROCEDURES

5.1 The chromatography system's method integration parameters must be optimized to the greatest extent possible so compounds are properly identified and integrated with minimal operator intervention. (Note: even when integration parameters work properly for calibration standards, the analyst must ensure the integration is appropriate on all samples. The analyst must not assume that the chromatography system will automatically apply the correct integration). When manual integrations are necessary to identify peaks as targets (determine the RT), the calibration standards must be reprocessed after updating the retention times to demonstrate that the data system integration parameters are set properly. The following steps are required:

5.1.1 Process the file using the current data system parameters for the mid-level standard.

5.1.2 Identify all of the target compounds and assign the correct RT to each target. Manual integrations at this point do not have to be documented and must not be included in the calibration evaluation.

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5.1.3 Reprocess the data and confirm that all of the targets can be identified and properly integrated. If the targets cannot be identified and properly integrated, adjust the integration parameters and reprocess the data. This is an important step. If the data system cannot reliably detect and integrate the targets in the mid-level standard, the probability of properly identifying and quantifying the targets in the remaining standards and samples are low.

5.1.4 Process the remaining calibration standards and confirm that the data system can routinely and properly identify the target compounds at each calibration level. Pay particular attention to the lowest level standard because this standard typically defines the reporting limit (RL). The integration parameters should allow for detection of the target compounds down to the quantitation limit or reporting limit.

5.1.5 The integration parameters set at the initial calibration must remain in use until the next calibration is performed, except as noted in 4.3. Manual integrations are used only when the conditions listed in Section 3.0 are encountered. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system.

5.1.6 Any manual integration of a chromatographic peak or group of peaks must be documented. In all instances where the data system report has been edited or where manual integration has been performed, the chromatographic system operator must clearly identify such edits or manual procedures as listed below:

- Manual integrations indicated on expanded scale "after" chromatograms.
- Re-integration technique marked, if available, on the data system
- Technical justification for manual integration.
- Analyst's initials and date. (data system application of analyst name or initials is acceptable so long as the data system allows the analyst to log in as himself or herself and has password control)

5.1.7 Project specific, client, program or STL laboratory specific requirements for manual integration may exceed the requirements of this policy. In those instances, the more specific requirements will apply or written approval allowing a deviation from the requirement must be received. For example:

- Requiring the before and after printing of the chromatograms
- Handwritten or electronic initialing and dating the changes made to the report
- Hardcopy printout of the EICP of the quantitation ion displaying the manual integration included in the raw data for all standards and samples, this applies to internal standards and surrogates as well.
- Requiring manual integrations to be documented in the project or case narrative

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5.2 Data reviewers shall confirm that documentation of manual integration is complete and that each manual integration is appropriate. This inspection shall be documented. At a minimum, the information required in Section 5.1.6 must be reviewed.

5.3 If integration indicates problems with analytical instrumentation, investigate the problem and take action to correct it. If poor chromatography routinely interferes with the ability to identify and quantify components; is a result of delayed system maintenance; and is not inherent in the system, such as (benzoic acid for Method 8270; benzo(b)anthracene and benzo(k)anthracene merging with column age; and dichlorobutenes merging with column age), then instrument maintenance must be performed. If instrument and data conditions have changed such that the default integration parameters no longer work as effectively, it is acceptable to change the default parameters and reprocess all affected data, including the associated standards, lab QC, and field samples, using the new integration parameters. Further manual manipulations after this reprocessing must be treated as manual integrations. The reason for reprocessing must be documented and approved.

5.4 Manual integrations on some data systems (e.g., Multichrom) may consist of adjusting integration parameters on a by-sample basis. Changes such as these must be documented.

5.5 Any deficiencies must be resolved with the analyst or their supervisor before the results are approved and released from the analytical department. Any questions arising from review of the documentation must be investigated in the electronic record, when available, prior to data acceptance. Any failures to complete these requirements shall be described in a non-conformance report.

5.6 Any concerns about violations of this policy must be reported to the facility Quality Manager, Laboratory Director or the Corporate Quality Director.

5.7 Electronic data surveillance is performed using *Mint Miner*™ Software. This software allows the user to connect to a workstation or archived data source and evaluate the audit trails in the electronic data file (refer to WI-STL-002/A-08/03).

6.0 DEFINITIONS

- Integration: The determination of the area or height under a curve (peak).

- Manual integrations: Include any adjustments to measurements of analytical peaks not applied equally to all applicable samples and QC parameters in an analytical batch by the data acquisition system. For the purpose of this policy, a manual integration has been performed if results for any of the analyses could not be duplicated by another analyst using the indicated calibration and standard peak integration protocol. Manual adjustments to peaks can include baseline changes, retention time window adjustments, changes to peak identification in samples (calibration standards' changes as required are exempt), manual peak height measurements, or changes to the formula used to

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model analytical peak areas or changes to background subtraction algorithms for GC/MS tuning. Although the latest analytical instruments are equipped to perform automatic integrations, manual integrations are sometimes necessary to accurately analyze samples if peaks are poorly resolved, exhibit tailing, the baseline drifts or is noisy, or other similar situations.

- Chromatograms: In the context of this policy, chromatograms are not necessarily limited to the output of chromatography instruments or automated data systems. They can include strip charts, integrator printouts, computer screen dumps, or any graphic display of a continuous signal from an analytical detector.

- Chromatography: A separation technique involving differential retention of components between stationary and mobile phases.

- Baseline: The chromatographic signal plotted as a function of time in the absence of signal construction from components of interest.

- Peak: An increase in signal from baseline to a maximum and then back to baseline.

- Coelution: the concurrent elution of two or more compounds to the detector at the same time.

- Elution: The process of movement of compounds from the chromatographic system.

- "Wavy" Baselines: A "wavy" baseline can be caused by minor impurities in carrier gas or solvent.

- Negative Spikes: Negative spikes in chromatograms are sudden upsets in chromatographic signal below the normal baseline.

- Sudden Rise in Baseline: A rise in the baseline is caused by several factors including high concentration of components in the sample and by normal column bleed.

- Carry-over: Carry over results from system contamination from previous analyses and results in signal unrelated to the current analysis.

- Peak Tailing: Peak tailing is a delayed return of a peak to chromatographic baseline and could be related to a delay of compound elution from the chromatographic system by adsorption or dead volume effects.

- Interference Peaks or Fused Peaks: Peaks that partially or totally coelute with the peak of interest.

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7.0 APPENDICES

- Appendix I. Examples of Peak shape and Proper integration Documenting Manual Integrations
- Appendix II. Examples of Improper Integration and Inflection Point Guidance

8.0 TRAINING MODULE

- Acceptable Manual Integration Practices, September 2004, Version 1.1: T-Q-004.

9.0 REVISION HISTORY

- Revision 1; dated 12/1/01
- Revision 2; Amended Section 5.7; dated 9/17/04.

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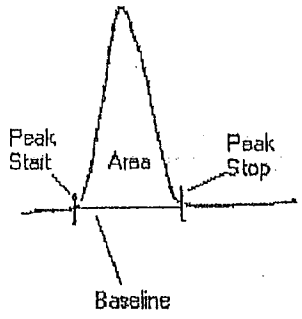
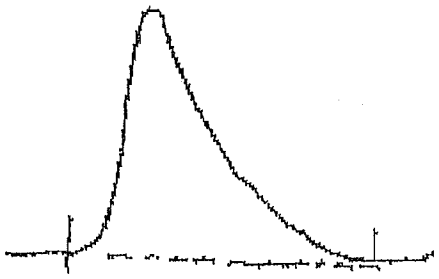
Appendix I.

Examples of Peak shape and Proper integration Documenting Manual Integrations

Ideal peak (Gaussian Shape) The start of integration is where the peak begins to rise from the background, and the end is where the peak returns to background.	
Tailing Peak Tailing peaks result from surface adsorption effects or dead volume in the instrument. When integrating tailing peaks, include only and all area that can be attributed to compound. If the baseline rises, the integration line should rise with the baseline.	

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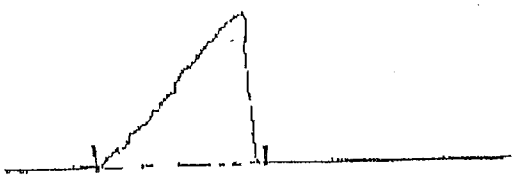
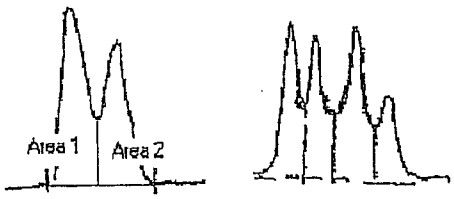
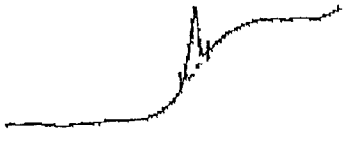
Fronting Peak Fronting peaks generally result from column overload and/or overcapacity. An example is benzoic acid on a 5% phenyl phase. In some cases, it is inherent in the analysis, in others, it is indicative of problems in the system. The analyst must have knowledge of their system. To integrate these peaks, it is important to have prior knowledge of how the compound acts when overloading versus co-eluting with a contaminate peak.	
Fused Peaks Fused peaks are near coeluters with some separation. They will occur in calibration mixes as well as real samples. To integrate, split the components with a vertical drop from the valley to the baseline.	
Hydrocarbon Envelope For semivolatile hydrocarbon analysis, most fuels produce "humpograms" like this one. Integration shall be performed in accordance with method, program or client specific requirements.	
Peak on a Baseline Rise Aside from hydrocarbon analysis, which uses the total area within a window for quantitation, baseline variations are not integrated. Therefore, skim the baseline rise to integrate the peak properly.	

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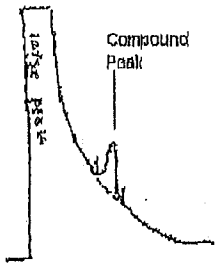
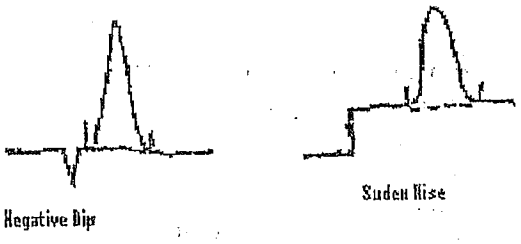
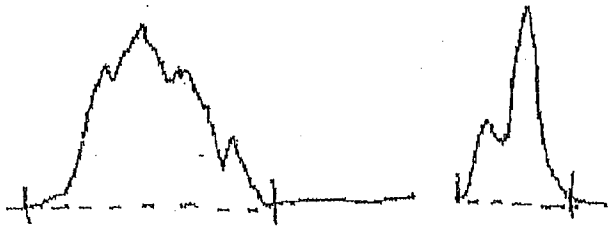
Skimmed Peak Use the tangent skimming functions of the integration software to correctly integrate small peaks on the tails of big peaks. Dropping vertical integration lines to the baseline of the big peak adds extra area which is not a part of the small peak, and results in high bias.	
Peak near a baseline upset Negative dips are common in ECD analysis, and the sudden rises in baseline are common with programmable fluorescence detectors where gain/wavelength switching occurs. Often, the default integration will go from the base of the negative peak to the far side of the peak of interest. This is results in high bias and is incorrect. Similarly, a default integration using the low part of the baseline rise and the far side of the peak of interest will also result in high bias and must be corrected.	
Split Peak Particularly in GC/MS analysis, low-level peaks may appear jagged or split. To integrate these properly, the analyst must have prior knowledge of the peak/compound chromatography.	

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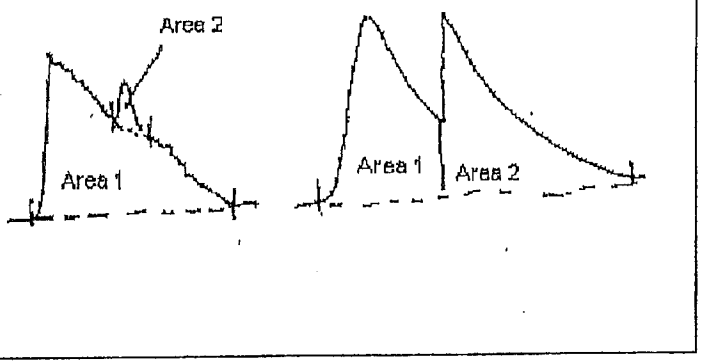
Fused tailing peaks These are very difficult to accurately quantify. It is best to do maintenance on the chromatography system to avoid this situation. To integrate these properly, the analyst should have prior knowledge of the compounds of interest. It is important to be consistent when integrating standards and samples.	

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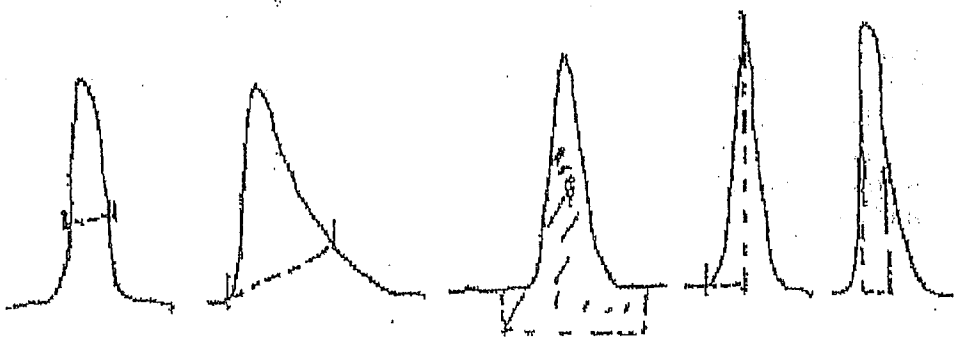
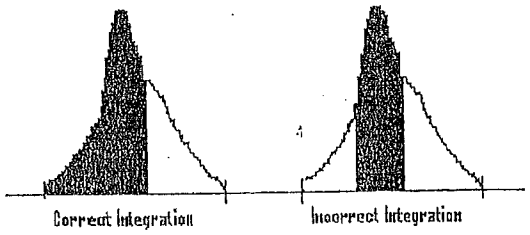
Appendix II.

Examples of Improper Integration and Inflection Point Guidance



An inflection point must be apparent when and if an integration point is drawn. For example:



When MS data has an inflection point in a peak, as shown in the example above, checking the underlying spectrum may be necessary to correctly manually integrate. On some chromatographic columns, for example, allyl chloride and carbon disulfide elute very close to each other, and they both share the primary characteristic ion mass 76. For both compounds mass 76 is the quantification mass. If two compounds can not be separated and a fused peak is going to be split at the inflection point, this can be correctly verified by looking at the spectra for each scan. In this example, the 76 peak may be fused, but the secondary ions will indicate which compound is present (carbon disulfide with secondary ion 78 and allyl chloride with secondary ions 41, 39 and 78).

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Severn Trent Services - Chicago
GC/MS BNA Case Narrative

[redacted]

JOB Number: 237518
BNA DATA: PAH's

1. All extractions and analyses were performed within recommended hold-times.

2. The MB (Method Blank) sample had all analytes below the CRQL (Contract Required Quantitation Limits).

3. LCG 5.0 QC limits were used as QC evaluation for the LCS (Laboratory Control Sample). The LCS had all spike recoveries within the QC limits. The ICALCHECK had all controlled spike recoveries within the 70-130% limits.

4. A MS/MSD (Matrix Spike/Matrix Spike Duplicate) was performed on sample -8. LCG 5.0 QC limits were used as QC evaluation for the MS/MSD samples. The MS/MSD recoveries and RPD values were within the QC limits.

5. The sample -2 had one surrogate below the QC limit, but greater than ten percent. No corrective action was required. All other samples had all surrogate recoveries within the LCG 5.0 QC limits.

=> 6. All manual integrations were summarized in the Manual Integration Summary Report.

7. MRL verification standards were analyzed before and after all samples. The first and last MRL standards for MRL 135973 had one compound above the QC limits, and all compounds detected in the DLCK standard.

8. The initial calibration had one compound (Benzo (g,h,i) perylene) above >20 % RSD but <30 % RSD. The calibration verification standard had all controlled compounds < 30% D as stated in the QAPP.

9. All analyses were performed following USEPA SW846 8270C protocol. The MS had two internal standards above the QC limit. No corrective action was required for two high internal standards in spiked samples. All other samples had all internal standard areas and retention times within the SOP acceptance limits as compared to the corresponding midpoint of the initial calibration standard.

Gary Rynkar
GC/MS Section Manager

7/13/5
Date

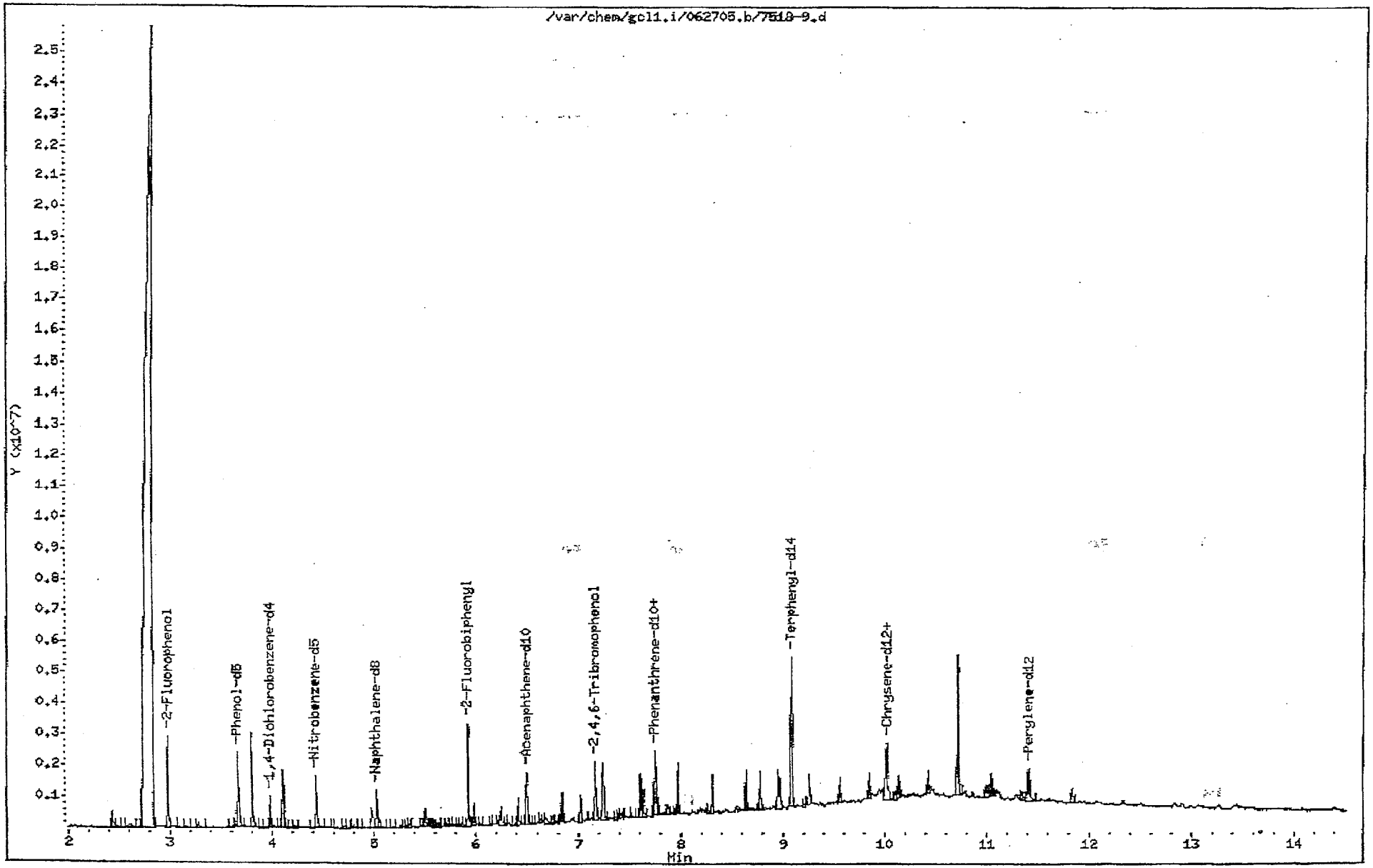
MANUAL INTEGRATION SUMMARY REPORT

Sample Name	Data File	Client ID	Compound
237518-16	062705.b/7518-16.d		Benzo(a)anthracene
237518-16	062705.b/7518-16.d		Chrysene
237518-4	062705.b/7518-4.d		Benzo(a)anthracene
237518-4	062705.b/7518-4.d		Chrysene
237518-5	062705.b/7518-5.d		Chrysene
~~237518-6~~	~~062705.b/7518-6.d~~		~~Benzo(a)anthracene~~
~~237518-6~~	~~062705.b/7518-6.d~~		~~Chrysene~~
237518-7	062705.b/7518-7.d		Benzo(a)anthracene
237518-7	062705.b/7518-7.d		Chrysene
237518-9	062705.b/7518-9.d		Benzo(k)fluoranthene
237518-10	062705.b/a7518-10.d		Benzo(a)anthracene
237518-10	062705.b/a7518-10.d		Chrysene

GP 7/13/5

Data File: /var/chem/gc11.i/062705.b/7518-9.d
Date : 27-JUN-2005 07:23
Client ID: GI02-DPS-10-5
Sample Info: 237518-009Y
Volume Injected (uL): 1.0
Column phase:

Instrument: gc11.i
Operator: GMO
Column diameter: 2.00



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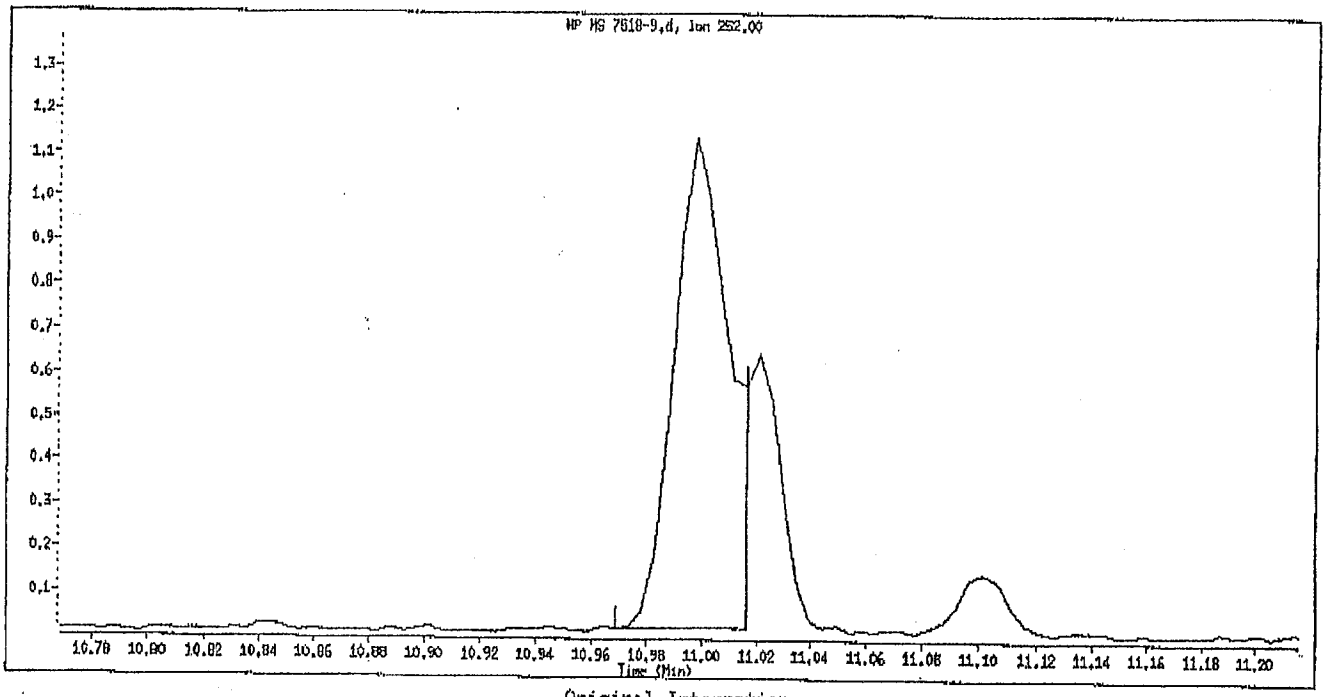
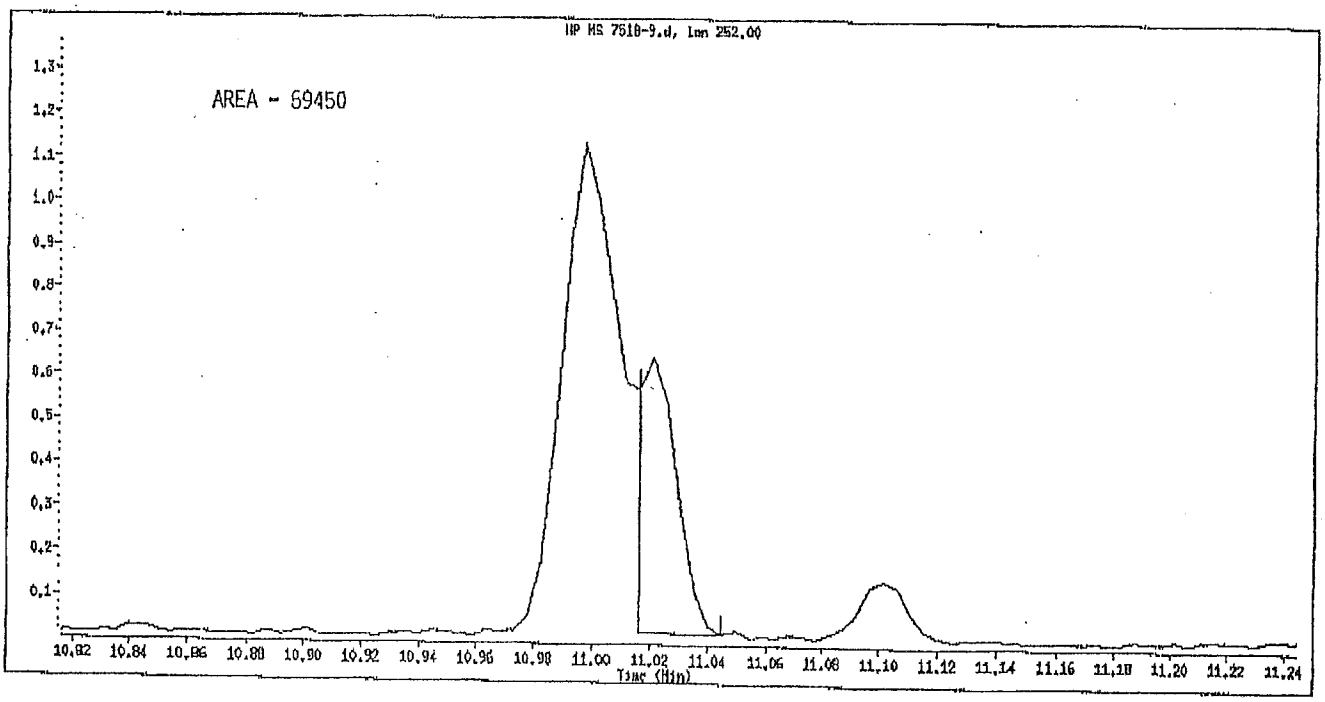
Data File Name: /518-9.d
Inj. Date and Time: 27-JUN-2005 07:23
Instrument ID: gc11.i
Client ID: GI02-DP5-10 5
Compound Name: Benzo(k)fluoranthene
CAS #: 207-08-9
Report Date: 07/12/2005



Original Integration



Manual Integration

Manually Integrated By: rynkarg
Manual Integration Reason: M5 Misintegration of peak by the Data System GR 7/13/5

Semivolatile REPORT SW-846 Method 8270C

Data file : /var/chem/gcl1.i/062705.b/7518-9.d
Lab Smp Id: 237518-9 Client Smp ID: GI02-DPS-10-5
Inj Date : 27-JUN-2005 07:23
Operator : GMO Inst ID: gcl1.i
Smp Info : 237518-009Y
Misc Info : 237518-9 062705.b
Comment : HP 6890 SERIES II GC/HP 5973 MS
Method : /var/chem/gcl1.i/062705.b/8270-1.m
Meth Date : 12-Jul-2005 14:41 rynkarg Quant Type: ISTD
Cal Date : 22-JUN-2005 16:41 Cal File: 1i0622h.d
Als bottle: 20
Dil Factor: 1.00000
Integrator: HP RTE Compound Sublist: PAH.sub
Target Version: 3.50
Processing Host: manatee

Concentration Formula: Amt * DF * Uf * Vt/(Vi * Ws * (100 - M)/100) * CpndVaria

Name	Value	Description
DF	1.00000	Dilution Factor
Ws	15.72500	Weigth of sample extracted (g)
Vt	500.00000	Volume of final extract (uL)(1000 low, 2
Vi	1.00000	Volume injected (uL)
M	11.30000	% Moisture
Uf	1.00000	ng unit correction factor

Cpnd Variable Local Compound Variable

GC 7/13/5

Compounds	QUANT SIG MASS	RT	EXP RT	REL RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng)	CONCENTRATIONS FINAL (ug/Kg)
* 22 1,4-Dichlorobenzene-d4	152	3.978	3.973	(1.000)	121097	8.00000	
* 51 Naphthalene-d8	136	5.029	5.024	(1.000)	498610	8.00000	
* 86 Acenaphthene-d10	164	6.498	6.498	(1.000)	300825	8.00000	
* 118 Phenanthrene-d10	188	7.754	7.749	(1.000)	662220	8.00000	
* 151 Chrysene-d12	240	10.022	10.017	(1.000)	460155	8.00000	
* 167 Perylene-d12	264	11.411	11.396	(1.000)	282830	8.00000	
$ 37 Nitrobenzene-d5	82	4.425	4.429	(0.880)	430562	21.4445	768.73
$ 72 2-Fluorobiphenyl	172	5.923	5.918	(0.911)	953907	20.6183	739.11
$ 137 Terphenyl-d14	244	9.080	9.076	(0.906)	1281036	25.3577	909.00
87 Acenaphthene	154	Compound Not Detected.					
134 Pyrene	202	8.971	8.966	(0.895)	315478	4.27487	153.24
52 Naphthalene	128	5.048	5.043	(1.004)	30565	0.53029	19.009
84 Acenaphthylene	152	Compound Not Detected.					

	Compounds	QUANT SIG MASS	RT	EXP RT	REL RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng)	CONCENTRATIONS FINAL (ug/Kg)
99	Fluorene	166	Compound Not Detected.					
119	Phenanthrene	178	7.773	7.773	(1.002)	146329	2.00340	71.816
120	Anthracene	178	7.816	7.815	(1.008)	22643	0.30545	10.950
130	Fluoranthene	202	8.776	8.771	(1.132)	408157	4.82501	172.96
152	Benzo(a)anthracene	228	10.013	10.008	(0.999)	147532	2.00995	72.051
154	Chrysene	228	10.046	10.046	(1.002)	152152	2.32236	83.250
163	Benzo(b)fluoranthene	252	10.997	10.992	(0.964)	161936	3.23832	116.08
164	Benzo(k)fluoranthene	252	11.021	11.021	(0.966)	59460	1.29779	46.522(M)
166	Benzo(a)pyrene	252	11.349	11.344	(0.995)	91264	2.20047	78.881
174	Indeno(1,2,3-cd)pyrene	276	12.828	12.823	(1.124)	81961	1.88749	67.661
175	Dibenzo(a,h)anthracene	278	12.837	12.842	(1.125)	36252	1.00907	36.172
176	Benzo(g,h,i)perylene	276	13.261	13.256	(1.162)	78157	2.37539	85.161
~~62~~	~~2-Methylnaphthalene~~	~~142~~	~~5.623~~	~~5.618~~	~~(1.118)~~	~~37855~~	~~0.98733~~	~~35.393~~

07/13/05

QC Flag Legend

M - Compound response manually integrated.

Appendix A.

Requirements for DOD QSM Version 3.0

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Organics (GC/MS)

QC Check	Definition	Purpose	Evaluation
Breakdown Check 8081A: Endrin, DDT 8270C: DDT	Analysis of s standard solution containing Endrin and DDT. Area counts of these compounds and their breakdown products are evaluated to assess instrument conditions.	To verify the inertness of the injection port because DDT and Endrin are easily degraded in the injection port.	If degredation of either DDT Endrin exceeds method-specified criteria, corrective action must be taken before proceeding with calibration
Confirmation of positive results (organics only)	Use of alternative analytical techniques (another method, dissimilar column, or different detector such as MS detector) to validate the presence of target analytes identified	To verify the identification of an analyte	This is a required QC procedure. All positive results must be confirmed.
CCV	This verification of the initial calibration that is required during the course of analysis at periodic intervals. Continuing calibration applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models	To verify that instrument response is reliable, and has not changed significantly from the current ICAL	If the values for the analytes are outside the acceptance criteria, the initial calibration may not be stable. Results associated with out-of-control CCV results require reanalysis or flagging
Demonstrate Acceptable Analyst Capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision	To establish the analysts' ability to produce data of acceptable accuracy and precision	The average recovery and standard deviation of the replicate must be within designated acceptance criteria.
Duplicate Sample	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are taken and prepared and analyzed identically.	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intralaboratory analytical process for a specific sample matrix	To provide information on the heterogeneity of the sample matrix. The greater the heterogeneity of the matrix, the greater the RPD between the sample and the duplicate
ICAL	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method	To establish a calibration curve for the quantification of the analytes of interest	Statistical procedures are used to determine the relationship between the signal response and the kn concentration of analytes of i The ICAL must be successful before any samples or other QC check samples can be analyzed.
Internal Standards	A known amount of standard added to all standards and samples as a reference for evaluating and controlling the precision and bias of the applied analytical method	To verify that the analytical system is in control	Any sample associated with out-of-control results must be reanalyzed.
LCS containing all analytes required to be reported	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern.	To evaluate method performance by assessing the ability of the lab/analyst to successfully recover the target analytes from a control (clean) matrix.	This is a required QC Check. The inability to achieve acceptable recoveries in the LCS indicate problems with the accuracy/bias of the measurement system.
MS	A sample prepared by adding a know amount of targeted analyte(s) to an aliquot of a specific environmental sample	To assess the performance of the method as applied to a particular matrix	The lack of acceptable recoveries in the matrix spike often points to problems with the sample matrix. One test of this is a comparison to the LCS recoveries. If the corresponding LCS recoveries are within acceptable limits, a matrix effect is likely. The lab should not correct for recovery; only report the results of the analyses and the associated MS results and indicate that the results from these analyses have increased uncertainty
MSD	A 2nd replicate MS prepared in the lab, spiked with an identical, known amount of targeted analyte(s), and analyzed to obtain a measure of the precision of the recovery for each analyte	To assess the performance of the method as applied to a particular matrix and provide information of the homogeneity of the matrix.	When compared to the MS, the MS will provide information on the heterogeneity of the sample matrix.

Table B-1 Cont.			
QC Check	**Definition**	**Purpose**	**Evaluation**
MDL Verification Check	A low-level spike taken through the prep and analytical steps at approximately 2x the MDL used to verify that the laboratory can detect analytes at the calculated MDL	To validate the MDL on an ongoing basis	If the MDL verification check fails, reprep/reanalyze at a higher level to set a higher MDL or the MDL study must be repeated.
MB	A sample of a matrix similar to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results.	To assess background interferences or contamination in the analytical system that might lead to high bias or false positive data.	This QC is used to measure lab accuracy/bias. The MB could indicate whether contamination is occurring during sample prep and analysis. If analytes are detected > ½ RL, reanalyze or B-Flag results for all samples in prep batch. For common lab contaminants, no analytes detected > RL. See DoD Box D-5; & Sec. D.1.1.1
MDL Study	The process to determine the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.	MDLs must be established prior to sample analysis. The RL or LOQ is at least 3x the MDL. Used in combination with the MDL verification check to validate the MDL on an ongoing basis.
RT window position establishment for each analyte (chromatographic methods only)	Determination of the placement of the RT window (start/stop time) of each analyte or group of analytes as it elutes through the chromatographic column so that analyte identification can be made during sample analysis. This is done during the initial calibration	To idendify analytes of interest	Incorrect window position may result in false negatives, require additional manual integrations, and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified.
RT window verification for each analyte (chromatographic methods only)	A standard is used to verify that the width and position of the RT windows are valid so that accurate analyte identification can be made during sample analysis	To minimize the occurance of both false positive and false negative results at each calibration verification.	The peaks from the standard used are compared to the RT window established during the ICAL to verify that the analytes of interest still fall within the window.
Second source calibration verification	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration	The concentration of the 2nd source calibration verification, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. This independent verification of the ICAL must be acceptable before sample analysis can begin.
Surrogate spike (organic analysis only)	A pure substance with properties that mimic the analyte of interest. Surrogates are compounds unlikely to be found in environmental samples to evaluate analytical efficiency by measuring their % Recovery.	To assess the ability of the method to successfully recover specific non-target analytes from an actual matrix.	Whereas the MS is normally done on a batch-specific basis, the surrogate spike is done on a sample-specific basis. Taken with the information derived from other spikes (LCS; MS), the bias in the analytical system can be determined.
Tuning (MS methods only)	The analysis of a standard compound to verify the mass spectrometer meets standard mass spectra abundance criteria prior to sample analysis	To verify the proper working of the mass spectrometer	Proper tuning of the mass spectrometer must be verified prior to sample analysis

Notes:

1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-3: Organic Analysis by GC/MS - Methods 8260 and 8270

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
IDOC	Per Instrument/Analyst	DoD acceptance criteria if available; otherwise method specific criteria	Correct / Repeat for those analytes which failed criteria	NA
MDL	Annually or quarterly MDL Checks performed	40 CFR 136B; MDL verification checks must produce a signal at least 3x the instrument's noise level.	Run MDL check at higher level and set MDL higher or reconduct MDL study	NA
Tuning	Prior to calibration and every 12 hours during sample analysis	Refer to method specific ion criteria	Retune instrument and verify. Rerun affected samples	NA
Breakdown check DDT (8270C only)	Daily prior to analysis of samples	Degradation $\leq$ 20% for DDT (Benzidine & PCP should be present at their normal response and no peak tailing should be observed)	Correct problem then repeat breakdown check	NA
ICAL	Initial 5-point calibration prior to sample analysis	1. Average RF for SPCCs: VOCs - $\geq$ 0.30 for Chlorobenzene and 1,1,2,2-tetrachloroethane, $\geq$ 0.1 for chloromethane, bromoform, and 1,1-dichloroethane SVOCs - $\geq$ 0.050 2. RSD for RFs for CCCs: VOCs and SVOCs - $\leq$ 30% and one option below. **Option 1:** RSD for each analyte $\leq$ 15% **Option 2:** linear least squares regression: r $\geq$ 0.995 **Option 3:** non-linear regression: Coefficient of determination (COD) $r^2 \geq 0.99$ (6 points shall be used for 2nd order, 7 points shall be used for 3rd order)	Correct problem then repeat initial calibration	NA
2nd Source calibration verification	Once after each initial calibration	Value of 2nd source for all analytes within $\pm$ 25% of expected value	Correct problem and verify 2nd source standard. Rerun, if that fails, correct problem and repeat ICAL	NA
RT window position establishement for each analyte	Once per ICAL	Position shall be set using midpoint standard of the initial calibration curve	NA	NA
Evaluation of Relative RT (RRT)	With each sample	RRT of each target analyte in each calibration standard within $\pm$ 0.06 RRT units	Correct problem, then rerun ICAL	NA
Calibration verification (CV)	Daily, before sample analysis, and every 12 hours of analysis time	1. Average RF for SPCCs: VOCs - $\geq$ 0.30 for Chlorobenzene and 1,1,2,2-tetrachloroethane, $\geq$ 0.1 for chloromethane, bromoform, and 1,1-dichloroethane SVOCs - $\geq$ 0.050 2. %Difference for CCCs: VOCs and SVOCs - $\leq$ 20% D (Note: D = difference when using RFs or drift when using least squares regression or non-linear calibration) All calibration analytes must be within 20% D, with no individual analytes (except CCC's) > 25% D (DoD Version 2.2)	Correct problem, rerun CV, if fails, repeat ICAL (Data associated with an unacceptable CCV may be fully usable under the following conditions: 1. CCV (high bias) and samples ND, then raw data may be reported with appropriate flag 2. CCV (low bias) and samples exceed maximum regulatory limit/decision level (DoD Box 60: Project specific permission from appropriate DoD personnel is required to report data generated from a run with noncompliant CCV.)	Apply J-flag to all results associated with the analytical batch for all analytes > 20%D and < 25% D. Identify in case narrative analytes > 20% D. (DoD Version 2.2) Apply Q-flag if no sample material remains and analyte exceeds criteria
Internal Standards verification	In all field samples and standards	RT $\pm$ 30 seconds from RT of the midpoint standard in the ICAL EICP area within -50% to +100% of ICAL midpoint standard	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory	Apply Q-flag to analytes associated with the non-compliant IS.
MB	One per prep batch	No analytes detected > ½ RL For common lab contaminants, no analytes > RL	Correct problem, then see criteria in box D-5; if required, reprep/reanalyze MB and all associated samples	Apply B-flag to all result for the contaminated analyte for all samples in the associated prep batch

Table B-3 cont.				
QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
LCS (containing all analytes to be reported)	One LCS per prep batch	DoD specified QC criteria, if available	Correct problem, reprep/reanalyze the LCS and all samples in the associated prep batch for all failed analytes, if sufficient sample is available	Apply Q-flag to specific analyte(s) in all samples in the prep batch.
MS	One per prep batch per matrix	For matrix evaluation, use DoD specified QC criteria for LCS	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample
MSD or Sample Duplicate	One per prep batch per matrix	RPD $\leq$ 30% (between MS and MSD or sample and sample duplicate)	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample
Surrogate	All field and QC samples	DoD specified QC criteria if available, otherwise method specific criteria or lab's own in-house criteria	For QC and field samples, correct problem, reprep/reanalyze all failed samples in the associated prep batch if sufficient sample material is available.	Apply J-flag for specific analyte(s) in all field samples collected from the same site matrix as the parent. Apply Q-flag to QC samples for specific analyte(s)
Results reported between LOD and LOQ			Apply J-flag to all results between LOD (MDL) and LOQ (RL)	
Manual Integration	When manual integrations are performed	Raw data shall include a complete audit trail for those manipulations, raw data output showing the results of the MI (i.e., chromatograms of manually integrated peaks), and notation of rationale, date, and signature/initials of person performing manual operation.		Apply M-flag to MI data

Notes:

1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

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TITLE: Metals Analysis Mercury by EPA Methods 245.1/245.5; SW-846 7470A/7471A; and U.S. EPA CLP Document No. ILM04.0

Updated by:	Signature:	Date:
George O. Klee Senior Analyst, Mercury	George O Klee	3-15-06

Approved by:	Signature:	Date:
Jodi L. Gromala Section Manager, Metals Dept.	Jodi L Gromala	3-14-06
David W. Mazur Env. Health & Safety Coor.	D W Mazur	3/15/06
Terese A. Preston Quality Manager	Terese A. Preston	3/15/06

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) outlines the digestion and analytical procedure for the determination of the mercury concentration in aqueous and non-aqueous media. This SOP was written using EPA 600/4-79-020 Methods 245.1 and 245.5; SW-846, 3rd Edition, Methods 7470A/7471A; and U.S. EPA CLP Document No. ILM04.0 as references.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

Specific requirements pertaining to the DoD QSM Version 3.0 are located in Attachment 3. These requirements are additionally applicable to all NFESC projects. Any deviations from these procedures and/or variances from must be addressed appropriately in accordance with standard operating protocol and pre-approved on a project by project basis.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Instrument Detection Limits

Instrument Detection Limits (IDLs) are performed quarterly for each element by the metals laboratory for each instrument as specified in CLP. These limits are used to gauge instrument sensitivity and when routinely evaluated, instrument performance without the introduction of method variance can be determined.

1.1.3 Reporting Limits

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the

respective MDL to ensure confidence in the value reported. Client specific requests for reporting to the IDL or MDL are special circumstances not to be confused with the previous statement.

Matrix	Reporting Limit [1]	CRDL [2]
Water	0.2 ug/L	0.2 ug/L
Soil	0.017 mg/kg	0.1 mg/kg

[1] Reporting Limit is used for EPA Method 245.1 and SW-846 7470A/7471A. Reporting Limits may vary depending on sample volume/size, dilution factors, and changes in the MDL.
[2] CRDL (Contract Required Detection Limit) is used for U.S. EPA CLP ILM04.0.

1.1.4 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM, Revision 03).

1.2 Summary of Method

This flameless cold vapor AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and swept from solution and passed through a cell of a double beam AA. Absorbance is a function of mercury concentration.

2.0 INTERFERENCES

- Chloride, sulfide and certain volatile organic materials.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

- Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the

information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 ppm in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Cmpds.	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.

1 – Always add acid to water to prevent violent reactions.
2 – Exposure limit refers to the OSHA regulatory exposure limit.

4.0 EQUIPMENT AND SUPPLIES

- 2 – Leeman Labs Model PS200 Automated Mercury Analyzer
- Class A volumetric glassware
- Eppendorf pipettes

5.0 REAGENTS AND STANDARDS

5.1 Reagents

5.1.1 Miscellaneous Reagents

- Hydrochloric Acid [HCl], Concentrated
- Nitric Acid [HNO_3], Concentrated
- Sulfuric Acid [H_2SO_4], Concentrated
- Deionized (DI) Water, Type II

5.1.2 Sodium Chloride-Hydroxylamine Hydrochloride Solution

Dissolve 240 g of sodium chloride and 240 g of hydroxylamine hydrochloride in sufficient DI water to make 2-liters of solution.

- Life of Reagent: 1 Year
- Storage Requirements: None

5.1.3 Stannous Chloride Solution

Dissolve 100 g of stannous chloride in 10% hydrochloric acid to make 1-liter of solution.

- Life of Reagent: 1 Month
- Storage Requirements: None

5.1.4 Potassium Permanganate, 5%

Dissolve 175 g of potassium permanganate into 3.5-liters of DI water.

- Life of Reagent: 1 Year
- Storage Requirements: None

5.1.5 Potassium Persulfate, 5%

Dissolve 175 g of potassium persulfate into 3,500 mLs of DI water.

- Life of Reagent: 1 Year
- Storage Requirements: None

5.2 Standards All standards are prepared in Class A volumetric flasks.

5.2.1 Standard Stock Solution I; 1,000 ppm

A 1,000 ppm concentrated mercury standard is purchased from an outside supplier.

- Life of Standard: 1 Year
- Storage Requirements: None

5.2.2 Working Standard Solution I; 100 ppb

To a 1.0 L volumetric flask filled with ~800 mLs DI water, transfer 100 uLs of Stock Solution I to the flask using a 100 uL Eppendorf pipette. Add 2.5 mLs conc. nitric acid as a preservative. Dilute to volume with DI Water. Invert and mix to insure complete mixture.

*For use in spiking Matrix Spikes, CRAs & the Standard Curve.

- Life of Standard: 24 Hours
- Storage Requirements: None

5.2.2.1 Working Standard Solution IA; 25 ppb

To a 100 mL volumetric flask filled with ~80 mLs DI water, transfer 25 uLs of Working Standard Solution I (Item 5.2.2) to the flask using an Eppendorf pipette. Dilute to volume with DI Water. Invert and mix to insure complete mixture.

*For use in spiking Matrix Spikes, CRAs & the Standard Curve in the **Hot Block Digester**

- Life of Standard: 24 Hours
- Storage Requirements: None

5.2.3 Standard Stock Solution II; 1,000 ppm

Purchased from an outside supplier as a 1,000 ppm solution and is from an alternate source than that of Standard Stock Solution I (Rgt. 5.2.1).

- Life of Standard: 1 Year
- Storage Requirements: None

5.2.4 Working Standard Solution II; 200 ppb

To a 1.0 L volumetric flask filled with ~800 mLs DI water, add 2.5 mLs concentrated nitric acid (as a preservative) and 200 uLs of Standard Stock Solution II to the flask (using a 200 uL Eppendorf pipette). Dilute to volume with DI water and invert several times to mix. *For use in spiking the ICV/CCV and LCS.

- Life of Standard: 24 Hours
- Storage Requirements: None

5.2.4.1 Working Standard Solution IIA; 50 ppb

To a 100 mL volumetric flask filled with ~80 mLs DI water, add 25 uLs of Working Standard Solution II (Item 5.2.4) to the flask using an Eppendorf pipette. Dilute to volume with DI Water. Invert and mix to insure complete mixture.

*For use in spiking the ICV/CCV and LCS in the **Hot Block Digester**

- Life of Standard: 24 Hours
- Storage Requirements: None

5.2.5 Working Standards for Mercury in Water

Standard (ug/L)	mLs of Working Soln. I or IA	Final Volume (mLs) Water Bath	Final Volume (mLs) Hot Block
Blank	0.0	100	25
0.2	0.2	100	25
0.5	0.5	100	25
1.0	1.0	100	25
3.0	3.0	100	25
5.0	5.0	100	25
CRA (0.2 ug/L)	0.2	100	25
Matrix Spike (1.0 ug/L)	1.0	100	25

Standard (ug/L)	mLs of Working Soln. II or IIA	Final Volume (mLs) Water Bath	Final Volume (mLs) Hot Block
Init. Cal. Verif. (ICV) (2.0 ug/L)	1.0	100	25
Cont. Cal. Verif. (CCV) (1.0 ug/L)	0.5	100	25
Lab Control Sample (LCS) (2.0 ug/L)	1.0	100	25

CLP Standard (ug/L)	mLs of Working Soln. II or IIA	Final Volume (mLs) Water Bath	Final Volume (mLs) Hot Block
Init. Cal. Verif (ICV) (2.0 ug/L)	1.0	100	25
Cont. Cal. Verif. (CCV) (1.0 ug/L)	0.5	100	25

NOTE: ILM04.0 requires the ICV and CCV to be at different levels.

5.2.6 Working Standards for Mercury in Soil (Block Digestion)

Standard (ug/L)	mLs of Working Soln. I	Final Volume (mLs) Hot Block
Blank	0.00	50
0.2	0.10	50
0.5	0.25	50
1.0	0.50	50
3.0	1.50	50
5.0	2.50	50
CRA (0.2 ug/L)	0.10	50
Matrix Spike (1.0 ug/L)	0.50	50

Standard (ug/L)	mLs of Working Soln. II	Final Volume (mLs) Hot Block
Init. Cal. Verif. (ICV) (2.0 ug/L)	0.50	50
Cont. Cal. Verif. (CCV) (1.0 ug/L)	0.25	50
Lab Control Sample (LCS) (2.0 ug/L)	0.50	50

CLP Standard (ug/L)	mLs of Working Soln. II	Final Volume (mLs) Hot Block
Init. Cal. Verif (ICV) (2.0 ug/L)	0.50	50
Cont. Cal. Verif. (CCV) (1.0 ug/L)	0.25	50

NOTE: ILM04.0 requires the ICV and CCV to be at different levels.

6.0 CALIBRATION (NON-DAILY)

All calibration procedures are performed on a daily basis. Refer to Section 7.4 for details.

7.0 PROCEDURE

7.1 Quality Control Checks

The following Quality Control samples are performed with each batch of samples. Refer to Section 8.0 for additional details.

QC Sample	Frequency [1]	Control Limits
Method Blank (MB)	1 in 20 samples	• < Reporting Limit (EPA / SW-846) • < CRDL (CLP)
LCS	1 in 20 samples	• 80-120% Recovery (EPA 245.5 / SW-846 / CLP) • 85-115% Recovery (EPA 245.1)
Matrix Duplicate (MD)[2]	1 in 20 samples	• 20 RPD unless the sample conc. is <5x RL, then ± RL. (EPA / SW-846) • 20 RPD unless the sample conc. is <5x CRDL, then ± CRDL. (CLP)

QC Sample	Frequency [1]	Control Limits
Matrix Spike (MS) MS Duplicate (MSD)[2]	1 in 20 samples	• 75 – 125% Recovery unless the sample concentration > spike level by 4x (EPA 245.5 / SW-846 / CLP) • 70 – 130% Recovery (EPA 245.1) • > 50% Recovery; if <50% Recovery, Method of Standard Additions (MSA) is required (TCLP)

[1] Drinking waters by EPA 245.1; and CLP analyses are analyzed at a frequency of 1 in 10 samples.
[2] The sample selection for MS/MSD or MS/MD, where appropriate, are rotated among client samples so that various matrix problems may be noted and/or addressed. MD's are performed only when requested by the client/project/contract. The MS/MSD are the routinely performed matrix QC indicators.

7.2 Sample Preservation and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times and preservations for the referenced programs.

Program	Preservation [1]	Holding Time [2]
SDWA	pH < 2, Cool 4 ± 2°C	28 days VTS [3]
CWA	pH < 2, Cool 4 ± 2°C	28 days VTS
RCRA	pH < 2, Cool 4 ± 2°C	28 days VTS
CLP	pH < 2, Cool 4 ± 2°C	26 days VTSR [4]

[1] Waters are preserved with nitric acid at pH <2; Soils are preserved at Cool 4 ± 2°C.
[2] Holding times include digestion and analysis.
[3] VTS: Verified Time of Sampling.
[4] VTSR: Verified Time of Sample Receipt.

7.3 Sample Preparation

7.3.1 Mercury Water Digestion Procedure - EPA Method 245.1 / CLP ILM04.0

Item	Full Scale (Water Bath)	Hot Block
Sample Volume	100 mLs	25 mLs
Reaction Vessel	BOD Bottle, 300 mLs	Sample Vials, 50 mLs
Sulfuric Acid (conc.)	5 mLs	1.25 mLs
Nitric Acid (conc.)	2.5 mLs	0.625 mLs
Potassium Permanganate, 5% Sol. (W/V)	15 mLs	3.75 mLs
Potassium Persulfate, 5% Sol. (W/V)	8 mLs	2 mLs
Preparation	2 hrs. @ 90 – 95°C, Cool	2 hrs. @ 90 - 95°C, Cool
Hydroxylamine Addition	6 mLs	1.5 mLs
Total Volume	136.5 mLs	34.125 mLs

NOTE: The sample should remain purple for 15 minutes after adding the potassium permanganate. It the sample does not maintain the purple color, a second addition of potassium permanganate is added to all samples of the batch to maintain the purple color.

Proceed with the Stannous Chloride addition.

7.3.2 Mercury Water Digestion Procedure - SW-846 Method 7470A

Item	Full Scale (Water Bath)	Hot Block
Sample Volume	100 mLs	25 mLs
Reaction Vessel	BOD Bottle, 300 mLs	Sample Vials, 50 mLs
Sulfuric Acid (conc.)	5 mLs	1.25 mLs
Nitric Acid (conc.)	2.5 mLs	0.625 mLs
Potassium Permanganate, 5% Sol. (W/V)	15 mLs	3.75 mLs
Potassium Persulfate, 5% Sol. (W/V)	8 mLs	2 mLs
Preparation	2 hrs. @ 90-95°C, Cool	2 hrs. @ 90 - 95°C, Cool
Hydroxylamine Addition	6 mLs	1.5 mLs
Total Volume	136.5 mLs	34.125 mLs

NOTE: The sample should remain purple for 15 minutes after adding the potassium permanganate. It the sample does not maintain the purple color, a second addition of potassium permanganate is added to all samples of the batch to maintain the purple color.

Proceed with the Stannous Chloride addition.

7.3.3 Mercury Soil Digestion Procedure - SW-846 Method 7471A

NOTE: Three aliquots of soils (~0.2 g) are combined and digested as one sample.

Item	Full Scale (Water Bath)	Hot Block
Sample Weight	~ 0.6 – 0.7 grams	~ 0.6 – 0.7 grams
Reaction Vessel	BOD Bottle, 300 mLs	Digestion Vessel
DI Water, Type II	5 mLs	2.5 mLs
Aqua Regia [3:1 HCl (conc.) to HNO_3 conc.)]	5 mLs	2.5 mLs
Preparation	2 min. @ 90-95°C, Cool	2 min. @ 90-95°C, Cool
DI Water, Type II	50 mLs	25 mLs
Potassium Permanganate, 5% Sol. (W/V)	15 mLs	7.5 mLs
Preparation	30 min. @90-95°C, Cool	30 min. @90-95°C, Cool
Hydroxylamine Addition	6 mLs	3 mLs
Total Volume	Dilute to 100 mLs	50 mLs

NOTE: The sample should remain purple for 15 minutes after adding the potassium permanganate. It the sample does not maintain the purple color, a second addition of potassium permanganate is added to all samples of the batch to maintain the purple color.

Proceed with the Stannous Chloride addition.

7.3.4 Mercury Soil Digestion Procedure - EPA Method 245.5 / CLP ILM04.0

Item	Full Scale (Water Bath)
Sample weight	0.2 - 0.3 grams
Reaction Vessel	BOD bottle, 300 mLs
Sulfuric Acid (conc.)	5 mLs
Nitric Acid (conc.)	2.5 mLs
Preparation	2 min. @ 90 -95°C, Cool
DI Water, Type II	50 mLs
Potassium Permanganate, 5% Sol. (W/V)	15 mLs
Potassium Persulfate, 5% Sol. (W/V)	8 mLs
Preparation	30 min. @ 90 - 95°, Cool
Hydroxylamine Addition	6 mLs
Total Volume	Dilute to 100 mLs

NOTE: The sample should remain purple for 15 minutes after adding the potassium permanganate. It the sample does not maintain the purple color, a second addition of potassium permanganate is added to all samples of the batch to maintain the purple color.

Proceed with the Stannous Chloride addition.

7.4 Calibration / Standardization

Before the instrument is used as a measurement device, the instrument response to known reference materials must be determined. All sample measurements must be made within this linear range of the instrument.

Standard	Frequency	Control Limit
Calibration Curve	Initially	Corr. Coeff. $\geq$ 0.995
ICV	After the Calibration Curve	• 90 –110% Recovery (EPA 245.5 / SW-846 / CLP) • 95 – 105% Recovery (EPA 245.1)
ICB	After the ICV	• < Reporting Limit (EPA / SW-846) • < CRDL (CLP)
CRA	After ICB	• No established limits.
CCV	Every 10 readings; end of each run	• 90 – 110% Recovery (EPA / CLP) • 80 – 120% Recovery (SW-846) (Note: The LabNet (LIMS) QC criteria code for the CCV is set at the default limit of 90-110% for all methods.)
CCB	Every 10 readings; End of each run	• < Reporting Limit (EPA / SW-846) • < CRDL (CLP)

7.4.1 Calibrating the System

The instrument must be calibrated before samples are analyzed.

To perform a calibration, go to the WinHg Runner and select the 'STANDARD' tab. Select the standards to be used by clicking on the S1, S2, S3, S4, S5 and S6 buttons. To set the number of replicates, click on the Rep1 button. Click on the 'Stnd Auto' button and the calibration will begin.

Reviewing the Calibration:
Go to the Database application by clicking the 'DB' button on the toolbar. Click on the 'Cal Curve' tab. Calibration data can be accepted by clicking the 'Accept' button.

7.4.2 Check Standards

This option allows for the verification that the calibration has not drifted. The Check Standards are placed in the tray with the samples to allow for AutoRun:

Positions 1-5: ICV, ICB, CRA, MB, LCS
Positions 11-12: CCV, CCB

To check standard concentrations:

- From the Main Menu, select CALIBRATION and then select CHECK STANDARDS. The check standard screen will appear.
- Type 1 for a check standard blank. Enter, in units specified on the standards page, the range of acceptance.
- Type 2 for check standards cup 2. Type the concentration and Enter. Type the percent acceptance and Enter.
- Repeat this for up to seven check standards.
- From Main Menu, select AUTOSAMPLES, then select SETUP and then check Enter the C1 frequency (e.g., 5/EPA protocol)
- Halt: Enter Y if the instrument should halt after an unacceptable check standard. Enter N for an alert only. Macros can be written to automatically recalibrate and rerun samples if check standards fall outside specifications.

7.5 Preventive Maintenance

The instrument requires some routine daily maintenance as well as some scheduled and non-scheduled periodic maintenance. All maintenance will be recorded in the instruments maintenance logbook. The following maintenance schedule lists the various maintenance procedures and when they should be performed. Each of these procedures is described in the following sections.

7.5.1 Maintenance Schedule

Equipment	Schedule
Drying Tube	Must be changed daily.
Pump Tubing	Weekly, or as needed.
Lamp	Replace as needed (avg. 4 mos. - 1 yr.).
Optical Cell	Clean as needed (typically monthly).
Liquid Gas Separator	Replace every 1-3 yrs., as needed.
Internal Tubing	Should not require replacement under normal circumstances.

7.5.2 Packing and Changing the Drying Tube

Under normal use, the drying tube must be changed each morning before analyzing samples. (The drying tube is located on the front panel on the left side of the instrument) Several tubes can be packed at one time and stored in an airtight container for a ready supply.

To pack a tube, plug one end with quartz wool, pour in magnesium perchlorate to fill tube, and plug the other end with quartz wool.

To change a tube, slightly loosen the nuts that hold the tube in at either end and slide the used tube out of the fittings. Slide a fresh tube into the fittings and tighten the fittings with your fingers to make a gas-tight seal.

To clean a tube, remove the quartz wool and the magnesium perchlorate. Either dispose of as a solid waste or dissolve in water and dispose of as a liquid waste. Clean the tube with ordinary laboratory glassware cleaner and dry thoroughly.

7.5.3 Replacing and Conditioning Pump Tubing

Pump Tubing should be replaced weekly or when it shows signs of wear. There are four pump tubes: two for drainage, one for sample, and one for reductant. Each tube is fed through a pump cassette which then clamps onto the pump head. Slide a tube through the plastic clips at the bottom of a cassette until the plastic tab is secure. Hold the tube taut, slide the loaded cassette onto the pump head, and lock the clamp up. Repeat for the remaining tubes, then connect the tubes ends.
For optimal performance, run DI water through new tubes for one hour to exercise them before using them for running samples. To do this, select INSTRUMENT from the Main Menu and then select OPERATION.

The INSTRUMENT:OPERATION screen will appear. Set the Pump Rate flow to the standard rate for 5 mL/min (Type R and M and 5 Enter). Wait for one hour and then connect the tubing to the appropriate fluids.

NOTE: This procedure only needs to be done once, when the tubes are new and unused.

7.5.4 Replacing the Lamp

The mercury lamp has a life of about 2000 hours, between four months and a year of use. The lamp needs to be replaced if the relative absorbance of a standard has changed significantly while the optical cell is clean. If the lamp is suspected, it is faster to replace the lamp and recalibrate than to clean the optical cell.

NOTE: Before installation, clean the new lamp quartz with methanol and wipe it dry. Do not get finger prints on the lamp and do not face the printing on the lamp toward the optical cell.

- Turn off the lamp (press the blue button on the front of the instrument).
- Remove the front panel of the instrument (lift up and out).
- Remove the optical assembly.
- Remove the two screws on the lamp housing and take off the lamp cover.
- Twist the lamp 90° and slide it straight out.
- Insert the new lamp and rotate it 90° in the reverse direction to secure it in place. Make sure that the lettering on the lamp will be facing to the left of the instrument when it has been reinstalled. If it is not, remove the lamp and reinsert it correctly.
- Replace the optical assembly.

7.5.5 Cleaning the Optical Cell

If the relative absorbance of standards differs significantly from that of previous calibrations, the optical cell (located inside the front panel) may be dirty and must be cleaned:

- Turn the lamp and the power off and remove the front panel by lifting it up and out.
- Remove the optics clamps, disconnect the detector, and rotate and lift out the assembly. Disconnect the gas lines.
- Remove the six screws holding the lamp spacer and the detector spacer onto the optical cell.
- Inspect the two ends with the lenses. If the external surface of the lenses appear to be the only contaminant, then clean. To clean use methanol. Install if no other cleaning is necessary.
- Disassemble the optical cell (using the allen wrench provided on the inside of the front cover) by removing (in order) the screws, lens, and gasket at each end.
- Carefully clean the inside of the cell with laboratory glassware cleaner, taking care not to scratch the inside surfaces. Rinse thoroughly, first with water and then with DI water. Dry the cell in the oven (free of contaminants) for one hour at approximately 40 - 50°C.
- Clean the lenses with laboratory glassware cleaner and rinse thoroughly with hot tap water. Flush lightly with methanol and dry by air or vacuum oven (maximum 50°C).
- Replace the gaskets (this is recommended although not required unless the gasket shows signs of wear) and reassemble the optical cell. Cleaning of the gaskets should only be done with DI water.

7.5.6 Replacing the Liquid Gas Separator

- The liquid gas separator (transparent block on the chemical panel) should only need to be replaced once every one to three years, depending on the amount of use it receives.
- To replace the separator, shut off the gas and liquid flow and flush the tubing with DI Water for safety purposes. Disconnect the four lines and remove the two screws. Remove the unit from the system, screw on a new one, reconnect the four lines, and turn the gas and liquid flow back on.

7.5.7 Replacing Internal Tubing

Internal gas and Teflon tubes should last indefinitely and should not need to be replaced. Periodically inspect all tubing for restrictions or blockages. If tubing should need to be replaced, do so one piece at time to avoid any confusion while making connections.

7.6 Sample Analysis

7.6.1 Preparing the System

The following procedures must be performed each morning before warming up the system:

- Change the drying tube. Refer to maintenance, Section 7.5 for instructions.
- Release the clamps and check the pump tubing for wear. Under normal use, the tubes will need to be replaced once a week. To replace the tubing, refer to maintenance, Section 7.5 for instructions.
- Check the reductant volume and refresh, if needed.
- Clean the rinse tank using standard lab cleaning practices, add fresh rinse.
- If the lamp has been off then turn on the lamp power and allow the lamp to warm up for at least 45 minutes.
- Start up the system.

7.6.2 Start-up Procedures

The start-up routine used will depend on the current state of the system. If it is in Overnite mode, use the Warmstart macro (15 minute warm-up). If the system has been completely powered down, run the Coldstart macro instead (3 hour warm-up).

7.6.3 Software Setup

- In order to run samples, enter all necessary information regarding the protocol, sample ID's, calibration values, and autosampler parameters into the software. This information is entered into a series of screens which are accessed from the Main Menu. (Display the Main Menu at any time by pressing the F1 key)

- Perform each of the following steps in sequence to set up the software. When these steps have been completed, the instrument will be able to run samples automatically.

NOTE: The steps below comprise the basic daily software setup sequence. The software also contains numerous advanced functions. Refer to the PS Series Reference Guide for a detailed description of the many other keys and functions available for use with this system.

7.6.4 Name the Protocol

From the 'Runner', click the toolbar button labeled 'DB' on the 'Database' command button on the 'Main' tab. From the 'Database', select 'File' from the pull down menu. Select 'New Protocol'. Enter a name in the 'Protocol Name' dialog box that appears. Select one of the check boxes in the 'Protocol type' group. This ensures the correct analytical conditions for the concentration range desired.

7.6.5 Name the Folder

Data set name is added from the WinHg Runner. Click on 'File' and select 'New Dataset'. 'Add New Batch' will pop up when you hit 'Enter'. New batch can also be added from the sample tab on the Runner.

7.6.6 Verify Values and Integration Times

Check to make sure that all values and integration times are correct for running the samples:

- From the Main Menu, select PROTOCOL, then select SET Values. The Set Values screen appears.
- For normal operation, enter the following values (as Illustrated below):

Number of Integrations:	1
Uptake time	10
Weight	N
Dilution	N
Percent Recovery	N

- Press F1 to return to the Main Menu.

7.6.7 Enter values for on/offs, times, and gains

All the information entered on the PROTOCOL tab on the WinHg database.

7.6.8 Enter the Calibration Standard Concentrations:

From the WinHg Database, select the 'Line Info' tab. Calibration standards and concentrations are entered here.

7.6.9 Reset the Calibration Intensity Data

The calibration can be reset from 2 different places. One option is from the WinHg Runner. Click the standards tab, then click on the 'New Cal Reset' button and 'OK'. Another option is from the WinHg Database. Click on the 'Cal Curve' tab and click the 4 buttons in the reset box.

7.6.10 Set the Autosampler Rinse Time

Pump rinse times and rates are setup in the protocol through the WinHg Database tab. Rinse is set at 50 seconds and the uptake is set at 10 seconds.

7.6.11 Set up the Racks

To launch the Rack Edit application, either click the 'Rack Editor' button the Runner 'Main' tab or click the Autosampler rack icon on the toolbar.

7.6.12 Define start-to finish sample sequence

Click on the 'Sample' tab on the WinHg Runner. In the 'Autosampler run' group, click on the combo box for Station 1 and select the rack to be run. Using the spin boxes, set the starting and ending cups. Click on 'Run Auto' to being analysis.

7.6.13 Running Samples

NOTE: Optimum Concentration Range = 0.2 ug/L - 5 ug/L

Once the rack and ranges are put in on the 'Autosample run' box on the sample tab, click the 'Run Auto' button to begin analysis.

7.6.14 Shutdown Procedures

There are two methods for shutting down the instrument. Under routine operation, when the system is used daily, only the lamp is shut off (system power remains on) and the Overnite routine is used to put the unit into a "sleep mode". If the system is to be completely turned off and not used for an extended period of time , or if it is to be shipped or moved, use the long-term Shutdown routine instead. These two methods are described below. For weekends or periods of "sleep" greater than 24 hours it is recommended to turn off the mercury lamp using the blue button.

NOTE: Before shutting down the instrument, the system must have beeped to indicate completion of the last procedure, and the word "Idle" should appear in the "State field in the top left of the displayed screen.

7.6.15 Short-Term (Overnite Macro)

Return to the WinHg Runner and click on the 'Control' tab. In the gas group, click on the 'Off' button, then in the 'Pump Group', click the 'Stand by' button. This will allow the instrument to autocycle to keep tubing clear of clogs.

7.6.16 Long-Term (Shutdown Macro)

For long-term shutdown, exit the software by selecting 'File' and then 'Exit' on the WinHg Runner pull-down menu.

7.7 Documentation

7.7.1 Instrument Run-Log

The analysis of samples and standards is documented within the instrument run log (Attachment 1) and supported by the instrument print-out. The runlog must be completed for each days analysis.

7.7.2 Traceability of Standards

Custom made and single element stock standard solution which are traceable to NIST or EPA are purchased. On receipt, each standard is recorded in LabNet (LIMS) and is issued a unique source ID#. The manufacturer, lot #, date received, expiration date, date of verification and the initials of the recording analyst are entered into the system.

7.7.3 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews according to the criteria established on the data review checklist (Attachment 2). Upon the first 100% review, the checklist is initialed and dated as reviewed. The package, with its review sheet, comments and any corrective action reports (CARs) is submitted to the supervisor, section manager, or peer reviewer for a second review. Once again, the checklist is initialed and dated by the second reviewer. The completed checklist remains on file with the original data.

8.0 QUALITY CONTROL

8.1 QC Summary

The laboratory generates annual statistically generated control limits and these can be used when requested by the client, contract or QAPP. These limits are based on the successive analysis of LCSs.

8.1.1 Calibration curve must be composed of a minimum of a blank and 5-standards. A least square fit linear calibration curve must have a minimum correlation coefficient of 0.995, which must be reported with the raw data.

8.1.2 ICV and ICB will be performed at the beginning of an analytical sequence. The ICV must not vary more than - a) 10% for EPA 245.5, SW-846 & CLP methods or b) 5% for EPA 245.1 method from its true value and must be prepared from a different source than the calibration curve standards.

Calibration verification will be performed with a CCV and CCB every 10 samples and at the end of the analysis. The CCV must not vary more than a) 20% for SW-846 methods or b) 10% for EPA & CLP methods from its true value and must be prepared from a different source than the calibration curve standards. (Note: The LabNet (LIMS) QC criteria code for the CCV is set at the default limit of 90-110% for all methods.) The CCB must be < Reporting Limit (EPA / SW-846) and < CRDL (CLP).

8.1.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve (dilute with a digested blank containing all reagents, or repeat the analysis using a smaller sample volume).

8.1.4 A minimum of one MB must be analyzed per sample batch to determine if contamination has occurred

8.1.5 An LCS will be included with each batch of 10 (drinking waters and EPA 245.1) or 20 (EPA 245.5, SW-846 or CLP) samples. The analyzed result must not vary more than 20% from the true value. For EPA Method 245.1, the LCS acceptance limits are 85-115%.

8.1.6 Matrix spike and duplicate samples are analyzed with each batch of 10 (drinking waters and EPA 245.1) or 20 (EPA 245.5, SW-846 or CLP) samples.

8.2 Corrective Actions

When an out-of-control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out-of-control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, section manager, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out-of-control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out-of-control situation should be reanalyzed. Out-of-control data must never be released without approval of the supervisor, section manager, project manager, QA personnel or the laboratory manager.

Listed below are steps that must be taken when an out-of-control situation occurs:

- demonstrate that all the problems creating the out-of-control situation were addressed
- document the problem and the action which was taken to correct the problem on a CAR
- document on the CAR that an in-control has been achieved and receive approval (signature) of the supervisor, section manager, QA personnel, or the laboratory manager prior to the release of any analytical data associated with the problem.

QC Indicator	Suggested Corrective Actions
Calibration Curve	• reanalyze the standard curve; • prepare a new stock and/or working standards; • check the reagents/solutions and prepare fresh if necessary.
Initial Calibration Verification (ICV)	• repeat ICV to verify proper preparation; • prepare new ICV from original stock; • recalibrate with a new standard curve; • prepare new stock and/or working standards; • check reagents/solutions and prepare fresh if necessary.
Initial Calibration Blank (ICB)	• prepare new ICB to verify proper preparation; • verify that the instrument base-line is stable and perform necessary maintenance, cleaning, etc.. to achieve stability; • determine the source of contamination by the process of elimination, carryover from a previous analysis or reagent contamination and correct the problem; • check reagents/solutions and prepare fresh if necessary; • correct for any contamination and reanalyze ICB and any associated samples.
Laboratory Control Sample (LCS)	If LCS is low: • reanalyze LCS to verify that it is out-of-control; • determine the source of error within the preparation procedure, repeat the sample set, write a CAR. If the LCS is high: • reanalyze LCS to verify that it is out-of-control; • determine the source of error within the preparation procedure, repeat the sample set; • determine if the high result is due to contamination; • check for contamination of reagents, LCS stock solution, or preparation area; • correct for contamination, reanalyze.
Method Blank (MB)	• reanalyze the MB to verify that it is beyond the reporting limit; • determine the source of contamination; • determine if the high result is due to contamination; • check for contamination of reagents or preparation area; • correct for contamination, reanalyze set; • in the extreme case where all samples in the set are at least 10X > the MB, reanalysis will not be required. However, a CAR and approval will be necessary.
Matrix Duplicate (MD)	• the sample must be reprocessed and reanalyzed; • if the reanalysis results in data that is still out of the control limit, then the sample will be ticked with a "*"; • regardless of the outcome of the reanalysis, a CAR will be written and approved by the Section Manager.
Matrix Spike (MS)	• the sample must be reprocessed and reanalyzed; • if the reanalysis results in data that is still out of the control limit, then the sample will be ticked with a "N"; • regardless of the outcome of the reanalysis, a CAR will be written and approved by the Section Manager.

QC Indicator	Suggested Corrective Actions
Continuing Calibration Verification (CCV)	• repeat CCV to verify proper preparation; • prepare new CCV from original stock; • check for instrument base-line drift or a change in one or more of the reagents; • check reagents/solutions and prepare fresh if necessary; • recalibrate with a new standard curve and repeat all samples since the previous in control CCV; • never dispose of any samples until you are sure that all QC, especially the CCV, are within the control limits.
Continuing Calibration Blank (CCB)	• prepare new CCB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc.. to achieve stability; • determine the source of contamination by the process of elimination, carryover from a previous analysis or reagent contamination and correct the problem, • check reagents/solutions and prepare fresh if necessary; • correct for any contamination and reanalyze CCB and any associated samples; • never dispose of any samples until you are sure that all QC, especially the CCB are within the control limits.
Summary	• If any of the ICV, ICB, CCV or CCB results are out-of-control for any element, the instrument is restandardized and the samples associated with the out-of-control elements are reanalyzed. • If the MB or LCS are out-of-control for any element, the samples are redigested. An exception is if the sample concentrations are $\geq$ 10X the MB contamination, the results are reported as is. • If any of the MD or MS results are out-of-control, a reanalysis is performed if there is sufficient sample. If there is insufficient sample, or the reanalysis is still out-of-control, the client is notified of the poor results via a case narrative that is sent with the data report. • CARs are available for out-of-control MB, LCS, MS and MD problems. These forms are completed by the analyst performing the analysis. The forms are then reviewed and signed by the supervisor or section manager. The signed forms are kept on file within the laboratory department and are used to prepare the case narrative (if applicable).

9.0 DATA ANALYSIS AND CALCULATIONS

Perform a linear regression or quadratic fit analysis of the calibration standard results. Compare sample results to the curve to determine the mercury concentration.

9.1 Water ug/L Hg = ug/L x Dilution Factor (Where L = Final digestate volume)

9.2 Soil $$\text{mg/kg Hg} = \frac{(\text{ug/L}) \times \text{L} \times \text{Dilution Factor}}{\text{wt(g)} \times \text{fraction solids}}$$

(Where L = Final digestate volume)

NOTE: All dry weight corrections are made in LabNet at the time the final report is prepared.

9.3 Accuracy

$$\%R = \frac{(A_T - A_O)}{A_F} \times 100$$

Where:
A_T = Total amount recovered in fortified sample
A_O = Amount recovered in unfortified sample
A_F = Amount added to sample

9.4 Precision

$$RPD = \frac{|C_1 - C_2|}{(C_1+C_2)/2} \times 100$$

Where:
C_1 = First measurement value
C_2 = Second measurement value

10.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by this Method

- Waste from this process goes into the "Corrosive Wastewater" wastestream.
- Single component standards should not be mixed into the waste streams unless approved by the Waste Coordinator. All standards with Hazardous constituents will be turned in to the waste technician for disposal.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0.

13.0 ATTACHMENTS

Attachment 1: Example: Instrument Maintenance Log and LIMS Forms
Attachment 2: Example: Data Review Checklist
Attachment 3: DoD QSM Version 3.0 Requirement Tables

Historical File:

Revision 00: 10/03/90
Revision 01: 08/09/91
Revision 02: 03/19/93
Revision 03: 10/18/95
Revision 04: 01/24/97
Revision 05: 03/31/99
Revision 06: 03/16/00
Revision 07: 05/23/01
Revision 08: 09/06/02
Revision 09: 03/29/04
Revision 10: 03/22/05
Revision 11: 03/15/06

Reasons for Change, Revision 11:

- Annual Review
- Addition of reference to DoD document in Section 1.0 and addition of DoD Tables in Attachment 3.

U:\QC\SOP\ME\UME-245.1.DOC

Attachment 1:

Example: Instrument Maintenance Log and LIMS Forms

STL Chicago
PS200 Leeman Mercury Analyzer – HG4
Instrument Maintenance Log

Page No._____

	Date/Initials	Date/Initials	Date/Initials	Date/Initials	Date/Initials	Date/Initials	Date/Initials
Daily Maintenance:							
Change Drying Tube							
Clean and Refill Rinse Tank							
Clean Sample Tip							
Check/Clean Optical Cell (Clean when reference intensity is <300,000)							

Weekly Maintenance:							
Change Pump Tubing							
Change Activated Carbon and Quartz Wool							

Comments:_____

_____

_____

_____

_____

Any Maintenance/Repair/Part Replacement performed that is not listed above must be documented in the Comments sections

Reviewer Signature:_____ Date:_____

Mercury (CVAA)
Method Code..: 245.1
Batch Code...: 175311

Status.....: RVWD
Batch Date...: 03/09/06
Batch Time...: 1529

User Name.....: gok
QC Code.....: 2007
Calc Code.....:

Location Code..: 57222
Equipment Code.: HG4
Import Code....:

			TEST CODE	H G
SAMPLE: Grp Pos	Sample ID	Dilution	TEST POS Date / Time	1
1 1	___S1_M05LSTK001_		3/8/06 1 1319	
1 2	___S2__		3/8/06 1 1322	
1 3	___S3__		3/8/06 1 1324	
1 4	___S4__		3/8/06 1 1326	
1 5	___S5__		3/8/06 1 1328	
1 6	___S6__		3/8/06 1 1331	
1 7	___ICV_M04LSTK010_		3/8/06 1 1333	0
1 8	___ICB__		3/8/06 1 1335	0
1 9	___CRA_M05LSTK001_		3/8/06 1 1337	0
1 10	___MB__		3/8/06 1 1339	0
1 11	___LCS_M04LSTK010_10		3/8/06 1 1341	0
1 12	244727_1____		3/8/06 1 1344	0
1 13	244727_2____		3/8/06 1 1346	0
1 14	___CCV_M04LSTK010_		3/8/06 1 1354	0
1 15	___CCB__		3/8/06 1 1356	0

*** QC Summary *** (V2)

Mercury (CVAA) Report Date: 3/27/06 10:44

ethod Code..: 245.1 Batch Date...: 03/09/06 QC Code.....: 2007 Equipment Code.: HG4
Batch Code...: 175311 Batch Time...: 1529 Calc Code.....: Import Code....:
Status.....: RVWD User Name....: gok Location Code..: 57222

Grp	Smp	Sample ID	Pos	Test	Result	Known	Original	Alternate	QC Res	F	QC Res	F
1	7	___ICV_M04LSTK010_	1	HG	1.999791	1000000			100			
1	8	___ICB__	1	HG	0.015518							
1	9	___CRA_M05LSTK001_	1	HG	0.232025	1000			116			
1	10	___MB__	1	HG	-0.00492							
1	11	___LCS_M04LSTK010_10	1	HG	2.090918	1000000	-0.00492		105			
1	14	___CCV_M04LSTK010_	1	HG	1.040618	1000000			104			
1	15	___CCB__	1	HG	-0.00346							

Mercury (CVAA) Report Date: 3/27/06 10:44

Method Code..: 245.1 Batch Date...: 03/09/06 QC Code.....: 2007 Equipment Code.: HG4
Batch Code...: 175311 Batch Time...: 1529 Calc Code.....: Import Code....:
Status.....: RVWD User Name....: gok Location Code..: 57222

SAMPLE:	Grp	Pos	Sample ID	Dilution	HG ug/L				
	1	1	___S1_M05LSTK001_		-1704				
	1	2	___S2__		4908				
	1	3	___S3__		16551				
	1	4	___S4__		33446				
	1	5	___S5__		110112				
	1	6	___S6__		174300				
	1	7	___ICV_M04LSTK010_		1.999791				
	1	8	___ICB__		0.015518				
	1	9	___CRA_M05LSTK001_		0.232025				
	1	10	___MB__		-0.00492				
	1	11	___LCS_M04LSTK010_10		2.090918				
	1	12	244727_1____		0.01022				
	1	13	244727_2____		0.013724				
	1	14	___CCV_M04LSTK010_		1.040618				
	1	15	___CCB__		-0.00346				

'A Digestion (Hg)
Method Code..: HGEPAD
Batch Code...: 175309

Status.....: RVWD
Batch Date...: 03/09/06
Batch Time...: 1525

User Name.....: gok
QC Code.....:
Calc Code.....: PREPFO

Location Code..: 57222
Equipment Code.: HG4
Import Code....:

SAMPLE: Grp	Pos	Sample ID	Dilution	TEST CODE / TEST POS Date / Time	DIGHG / 1
1	1	___S1_M05LSTK001_		3/8/06 1 1030	0
1	2	___S2__		3/8/06 1 1030	0
1	3	___S3__		3/8/06 1 1030	0
1	4	___S4__		3/8/06 1 1030	0
1	5	___S5__		3/8/06 1 1030	0
1	6	___S6__		3/8/06 1 1030	0
1	7	___MB__		3/8/06 1 1030	0
1	8	___LCS_M04LSTK010_7		3/8/06 1 1030	0
1	9	244727_1____		3/8/06 1 1030	0
1	10	244727_2____		3/8/06 1 1030	0
1	11	_____			

*** BATCH WORKSHEET *** (V2)

EPA Digestion (Hg) Report Date: 3/27/06 10:45

Method Code..: HGEPAD	Batch Date...: 03/09/06	QC Code.....:	Equipment Code.: HG4
Batch Code...: 175309	Batch Time...: 1525	Calc Code.....: PREPFO	Import Code....:
Status.....: RVWD	User Name....: gok	Location Code..: 57222	

BATCH:	Item	Description	Description Information
	1	Analyst:	GEORGE KLEE, JR.
	2	Reviewer:	
	3	Equipment ID:	1173
	4	Wavelength: 253.7nm Cell length: 20.5cm	
	5	Water Bath Temp: Initial(Limits 90C-95C)	
	6	Water Bath Temp: Final	
	7	Block Digestor Temp: Initial (90C-95C)	95
	8	Thermometer ID: Correction Factor:	1173 +2
	9	Repipettor Volume Check:	OK
	10	HNO3 Lot#:	A22035
	11	HCL Lot#:	5587 A06A22
	12	H2SO4 Lot#:	5557 A20A08
	13	KMnO4 Lot#:	7056 X49655
	14	SnCl2-H2O Lot#:	A40600
	15	NH2OH-HCL Lot#:	Y28599
	16	K2S2O8 Lot#:	T44H13
	17	NaCl Lot#:	43234351
	18	Date Sample Prepped:	03/08/06
	19	Prep Time In:	1030
	20	Prep Time Out:	1230

SAMPLE:	Grp	Pos	Sample ID	Dilution	DIGHG Text	MLI mL	MLF mL	WEIGHT g	PREPF N/A
	1	1	___S1_M05LSTK001_		Complete	25	25		1.0000
	1	2	___S2__		Complete	25	25		1.0000
	1	3	___S3__		Complete	25	25		1.0000
	1	4	___S4__		Complete	25	25		1.0000
	1	5	___S5__		Complete	25	25		1.0000
	1	6	___S6__		Complete	25	25		1.0000
	1	7	___MB__		Complete	25	25		1.0000
	1	8	___LCS_M04LSTK010_7		Complete	25	25		1.0000
	1	9	244727_1____		Complete	25	25		1.0000
	1	10	244727_2____		Complete	25	25		1.0000
	1	11	_____						

EPA Digestion (Hg) Report Date: 3/27/06 10:45

thod Code..: HGEPAD Batch Date...: 03/09/06 QC Code.....: Equipment Code.: HG4
Batch Code...: 175309 Batch Time...: 1525 Calc Code.....: PREPFO Import Code....:
Status.....: RVWD User Name....: gok Location Code..: 57222

SAMPLE:	Grp	Pos	Sample ID	Dilution	DIGHG Text	MLI mL	MLF mL	WEIGHT g	PREPF N/A

SAMPLE:	Grp	Pos	Sample ID	Dilution	DLFAC N/A	VOL mL			
	1	1	___S1_M05LSTK001_		1.0000	25			
	1	2	___S2__		1.0000	25			
	1	3	___S3__		1.0000	25			
	1	4	___S4__		1.0000	25			
	1	5	___S5__		1.0000	25			
	1	6	___S6__		1.0000	25			
	1	7	___MB__		1.0000	25			
	1	8	___LCS_M04LSTK010_7		1.0000	25			
	1	9	244727_1____		1.0000	25			
	1	10	244727_2____		1.0000	25			
	1	11	_____						

Attachment 2.

Example: Data Review Checklist

STL Chicago
INORGANIC CLP / LEVEL IV DATA REVIEW CHECKLIST

Site Name: _____ Primary Reviewer: _____ Review Date: _____
JOB Number: _____ Secondary Reviewer: _____ Review Date: _____
No. of Samples/Matrix: a) WATER _____ b) SOIL _____ c) TCLP / SPLP _____ d) OTHER _____

Metals List: a) TAL b) PP c) TCLP d) Other (_____)
Report Level: **IDL** = a) CLP b) Non-CLP c) MDL d) Other _____ **CRDL** = a) CLP b) Client c) Default RL d) Other

TASK : CAR's _____	PRI REV	SEC REV	COMMENTS
LAB CHRON: 1) Matches COC			
2) Proper Prep Links: S-F6 (Routine) S-F9 (TCLP/SPLP)			
3) Sample Hold Times Met			
Cyanide Reported on Forms	Y / N		Method: a) CLP b) SW846 9010B/9014
Initial / Continuing Calibration Criteria Met (CRA/CRI requirements met if applicable)			
FORM 1: Matches Report LabNet Report Units / Test Matrix Match Form 1's Dilutions due to interference's resulted in elevated RL's			
FORM 3: Method Blanks < CRDL			
FORM 5A: MS Recoveries Acceptable Default Limits _____ Statistical Limits _____ Project Limits _____ (S-F10 used to Clone By Project)			N
FORM 5B: PDS Performed			
FORM 6: Duplicate RPD Acceptable Default Limits _____ Statistical Limits _____ Project Limits _____ (S-F10 used to Clone By Project)			*
FORM 7: LCS Recoveries Acceptable Default Limits _____ Statistical Limits _____ Project Limits _____ (S-F10 used to Clone By Project)			^
FORM 8: MSA Analysis Performed			S
GFAA – Analytical Spike (AS) Recoveries Acceptable			W
GFAA – Repeat Analytical Recovery <40%			E
GFAA – Duplicate Injection Precision Met			M
FORM 9: Serial Dilution (SD) Acceptable			E
FORM 14's Correct			
RAW DATA: Complete (Match Batches to LabChron) a) Instr. Raw Data clearly displays the LabNet Batch number and includes the "Batch Worksheet" Report b) Prep Raw Data displays the LabNet Batch Number and includes the "Batch Worksheet" Report or "Raw Data" Report			

Comments on Reverse

TASK : CAR's _____	PRI REV	SEC REV	COMMENTS
LabNet Batch Status Report Displays Data At RVWD Status			
Incomplete JOB Status Report reveals no Outstanding Data			
NARRATIVE: 1) Holding Times			
2) Method References			Method: a) CLP b) SW846 c) Other
3) % Recoveries / RPD's			
4) Analytical Difficulties/Typos			

COMMENTS:

QC CYCLE	REASON
1	
2	

STL Chicago
Mercury Data Review Checklist: Automated CV (PS 200)

Instrument ID: HG3 HG4 (circle one) **LabNet Batch No.:**_____

Analyst Initial(s):_____ **Date:** _____

Copies: _____ _____
_____ _____
_____ _____
_____ _____
_____ _____

****

QC Type: a. CLP b. Standard c. TCLP d. Drinking Waters e. Solubles

I. Calibration:

Analyst Reviewer

1. Calibration is clearly documented.
   - ____ ____ a. c.c.: 0.995 to 1.000
   - ____ ____ b. y-intercept: **Std. QC**: < RL; **CLP QC**: < CRDL

2. Calibration Verification
   CLP QC: Every 10 Sample Bottles
   Std. QC: Every 20 Sample Bottles
   TCLP QC: Every 20 Sample Bottles
   Drinking Waters: Every 10 Sample Bottles
   - ____ ____ a. ICV/CCV **Std./SW-846:** ± 10% (ICV); ± 20% (CCV); (Note: CCV Default of +/-10% set in LabNet)
     CLP: ± 10% (ICV); ± 10% (CCV)
     EPA 245.1: ± 5% (ICV); ± 10% (CCV)
   - b. ICB/CCB **Std. QC**: < RL; **CLP QC**: < CRDL

3. CRA
   - ____ ____ **CLP QC**: At CRDL; Analyzed each Calibration; No Limit; **Std. QC**: At CRDL; Analyzed Daily; ± RL

II. Sample Analysis:

Analyst Reviewer

1. Each Preparation Batch:
   - ____ ____ a. Must be clearly identified
   - ____ ____ b. Contains a maximum of 20 samples
   - ____ ____ c. 1 Prep Blank: **CLP:** < CRDL; **Std. QC:** < RL
   - ____ ____ d. 1 LCS: **Std./CLP:** 80-120% Rec. **EPA 245.1:** 85-115% Rec.
   - ____ ____ e. 1 Matrix Spike: **Std./CLP:** 75-125% Rec.; ***Unless*** the sample conc. exceeds the spike conc. by factor 4x.
     TCLP: > 50% Rec.; If <50%, MSA analysis is required
     245.1: 70-130% Rec.
   - ____ ____ f. 1 Matrix Duplicate: **Std.:** RPD/RSD limits are 20% ***Unless*** the sample conc. is <5x RL then ± RL
     CLP: RPD or RSD limits are 20%; ***Unless*** the sample conc. is <5x CRDL then ± CRDL applies.
   - ____ ____ g. % TS for samples to be reported on a Dry Wt.

III. Data Documentation

Analyst Reviewer

1. ____ ____ The instrument and current conditions must be clearly documented. The Temperature of the Water Bath must be 95°C.
2. ____ ____ **All** Percent Recoveries and RPD's need to be documented in the raw data.
3. ____ ____ If the CCB/PB and/or CCV/LCS are outside of the control limits, **a CAR must be written** and the Section Manager or Unit Leader must be notified that redigestion is required.

STL Chicago
Mercury Data Review Checklist: Automated CV (PS 200)

III. Data Documentation (continued)

Analyst Reviewer

4. Matrix Spike outside the control limits:
   a. **CLP QC**: No corrective action required, the sample is ticked appropriately.
   b. **Std. QC**: **A CAR must be written** and the Section Manager or Unit Leader must make the decision as to whether re-digestion is required.
   c. If MSA is performed; check the calculation.
5. Sample Duplicate outside the control limits:
   a. **CLP QC**: Normally no corrective action required, and the result is ticked appropriately.
   b. **Std. QC**: **A CAR must be written** and the Section Manager or Unit Leader must make the decision as to whether redigestion is required.
6. The sample data and QC is recorded in the databook in the order in which they were analyzed. **All** unused data is clearly identified.
7. Standard Traceability is correctly documented.
8. Data Report accurately reflects the documentation in the Databook and the LIMS Spreadsheet.
9. The analyst's full signature is required on the following:
   a. Instrument Data Report
   b. Databook
   c. Data Review Checklist
   d. Print out LabNet Pages, Raw Data, QC, and RunLog
   e. Samples needing copying are clearly marked
10. All unused portions of the data page are Z'd out.
11. Proper Corrective Action Documentation for any out of control situation is clearly identified.

IV. Miscellaneous

Analyst Reviewer

1. Is Sample Prep Linked?
2. Is TCLP Linked? (Shift F9 from the start page)
3. Did all dilutions carry over for MD, MS, MSD (where applicable)?
4. Did all prep and analysis matrices match up?

Comments:_____

Analyst Signature: _____ Date: _____.

Reviewer Signature:_____ Date: _____.

Attachment 3.

DoD QSM Version 3.0 Requirement Tables

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Inorganics (Metals)

QC Check	Definition	Purpose	Evaluation
Calibration Blank (Metals only)	Reagent water containing no analytes of interest, but acidified to the same pH as all samples	To determine the zero point of the calibration curve for all initial and continuing calibrations	Continued calibration blank responses above 2x the MDL require corrective action
CCV	This verification of the initial calibration that is required during the course of analysis at periodic intervals. Continuing calibration applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models	To verify that instrument response is reliable, and has not changed significantly from the current ICAL	If the values for the analytes are outside the acceptance criteria, the initial calibration may not be stable. Results associated with out-of-control CCV results require reanalysis or flagging
Demonstrate Acceptable Analyst Capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision	To establish the analysts' ability to produce data of acceptable accuracy and precision	The average recovery and standard deviation of the replicate must be within designated acceptance criteria.
Dilution test (Metals only)	Analysis of a positive sample, which has been diluted to a concentration 1/5th of the original, to confirm that there is no interference in the original sample analysis.	To assess matrix interference	Agreement within 10% between the concentration for the undiluted sample and 5x the concentration for the diluted sample indicates the absenxe of interferences, and such samples may be analyzed without using MSA. Results outside acceptance limits indicate a possible matrix effect. ICP: must run a post-digestion spike GFAA: must run a recovery test
Duplicate Sample	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are taken and prepared and analyzed identically.	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intralaboratory analytical process for a specific sample matrix	To provide information on the heterogeneity of the sample matrix. The greater the heterogeneity of the matrix, the greater the RPD between the sample and the duplicate
ICAL	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method	To establish a calibration curve for the quantification of the analytes of interest	Statistical procedures are used to determine the relationship between th signal response and the known concentration of analytes of interest. The ICAL must be successful before any samples or other QC check samples can be analyzed.
IDL (6010 and 6020 only)	The process to determine the minimum concentration of a substance (analyte) that an instrument can differentiate from noise. The procedure for calculating varies by method.	To provide a quarterly evaluation of instrument sensitivity	IDLs must be established before samples can be analyzed.
Interference check solutions (ICP only)	A pair of solutions containing interfering elements that are used to verify the correction factors of analytes of concern	To verify the established correction factors by analyzing the interference check solution at the beginning of the analytical sequence	No samples can be run if this check does not pass acceptance criteria
LCS containing all analytes required to be reported	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern.	To evaluate method performance by assessing the ability of the lab/analyst to successfully recover the target analytes from a control (clean) matrix.	This is a required QC Check. The inability to achieve acceptable recoveries in the LCS indicate problems with the accuracy/bias of the measurement system.
Linear dynamic range or high-level check standards (ICP only)	High-level check standard periodically analyzed to verify the linearity of the calibration curve at the upper end	To verify quantitative accuracy of data up to the high-level standard	The QC check establishes the upper linear range of the calibration
Low-Level calibration check standard (ICP only)	A reference standard that contains a quantity of analyte (greater than or equal to 3x the LOD (MDL))	To confirm the accuracy of measurements at or near the LOQ (RL), It establishes the LOQ of the calibration curve for those ICP methods that rely on single point calibration. It also may be used to validate a client's project RL	This QC check must be within acceptance criteria before any samples are analyzed.

Table B-1 cont.			
QC Check	**Definition**	**Purpose**	**Evaluation**
MS	A sample prepared by adding a know amount of targeted analyte(s) to an allquot of a specific environmental sample	To assess the performance of the method as applied to a particular matrix	The lack of acceptable recoveries in the matrix spike often points to problems with the sample matrix. One test of this is a comparison to the LCS recoveries. If the corresponding LCS recoveries are within acceptable limits, a matrix effect is likely. The lab should not correct for recovery; only report the results of the analyses and the associated MS results and indicate that the results from these analyses have increased uncertainty
MSD	A 2nd replicate MS prepared in the lab, spiked with an identical, known amount of targeted analyte(s), and analyzed to obtain a measure of the precision of the recovery for each analyte	To assess the performance of the method as applied to a particular matrix and provide information of the homogeneity of the matrix.	When compared to the MS, the MSD will provide information on the heterogeneity of the sample matrix.
MDL Verification Check	A low-level spike taken through the prep and analytical steps at approximately 2x the MDL used to verify that the laboratory can detect analytes at the calculated MDL	To validate the MDL on an ongoing basis	If the MDL verification check fails, reprep/reanalyze at a higher level to set a higher MDL or the MDL study must be repeated.
MB	A sample of a matrix similar to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results.	To assess background interferences or contamination in the analytical system that might lead to high bias or false positive data.	This QC is used to measure lab accuracy/bias. The MB could indicate whether contamination is occurring during sample prep and analysis. If analytes are detected > ½ RL, reanalyze or B-Flag results for all samples in prep batch. For common lab contaminants, no analytes detected > RL. See DoD Box D-5; & Sec. D.1.1.1
MDL Study	The process to determine the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.	MDLs must be established prior to sample analysis. The RL or LOQ is at least 3x the MDL. Used in combination with the MDL verification check to validate the MDL on an ongoing basis.
MSA (ICP/GFAA only)	Adding known amounts of standard to one or more aliquots of the processed sample solution.	To compensate for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences that cause a baseline shift.	This is the method used when matrix interferences are present and do not allow determination of accurate sample results
Post digestion spike addition (ICP and ICP/MS only)	An analyte spike added to a portion of prepared sample to verify absence or presence of matrix effects	To confirm the presence of a matrix interference. Assess matrix effects based on: 1. the occurrence of new and unusual matrices included within the batch, or 2. contingency analysis based on SD or MS failures	To verify the absence of an interference, the spike recovery criteria is 75%-125% Results outside this criteria require MSA for all samples within the batch
Recovery Test (GFAA only)	An analyte spike added to a portion of prepared sample to verify absence or presence of matrix effects	To confirm the presence of a matrix interference. Assess matrix effects based on: 1. the occurrence of new and unusual matrices included within the batch, or 2. contingency analysis based on SD or MS failures	To verify the absence of an interference, the spike recovery criteria is 85%-115% Results outside this criteria require MSA for all samples within the batch

Table B-1 cont.			
QC Check	**Definition**	**Purpose**	**Evaluation**
Second source calibration verification	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration	The concentration of the 2nd source calibration verification, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. This independent verification of the ICAL must be acceptable before sample analysis can begin.

Notes:
1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

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DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-6: Inorganic Analysis by ICP and AA - Methods 6010 and 7000 Series

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
IDOC	Per Instrument/Analyst	DoD acceptance criteria if available; otherwise method specific criteria	Correct / Repeat for those analytes which failed criteria	NA
MDL	Annually or quarterly MDL Checks performed	40 CFR 136B; MDL verification checks must produce a signal at least 3x the instrument's noise level.	Run MDL check at higher level and set MDL higher or reconduct MDL study	NA
IDL (ICP only)	Every 3 months	Detection limits established shall be ≤ MDL	NA	NA
Linear dynamic range (LRS) or high-level check (ICP only)	Every 6 months	Within ± 10% of expected value	NA	NA
ICAL ICP: min 1 high std and a calibration blank GFAA: min 3 stds and a calibration blank CVAA: min 5 stds and a calibration blank	Daily initial calibration prior to sample analysis	ICP: No acceptance criteria unless more than 1 standard is used, in which case $r \geq 0.995$ GFAA: $r \geq 0.995$ CVAA: $r \geq 0.995$	Correct problem then repeat initial calibration	NA
2nd Source calibration verification (ICV)	Once after each initial calibration	Value of 2nd source for all analytes within ± 10% of expected value	Correct problem and verify 2nd source standard. Rerun, if that fails, correct problem and repeat initial calibration.	NA
Continuing Calibration verification (CCV)	CCV – After every 10 field samples and at end of analysis sequence. (DoD Box 58: CCV standards shall be at or below the middle of the calibration range)	ICP: within ± 10% of expected value GFAA: within ± 20% of expected value (Data associated with an unacceptable CCV may be fully usable under the following conditions: 1. CCV (high bias) and samples ND, then raw data may be reported with appropriate flag 2. 2. CCV (low bias) and samples exceed maximum regulatory limit/decision level (DoD Box 60: Project specific permission from appropriate DoD personnel is required to report data generated from a run with noncompliant CCV.)	Correct problem, rerun CCV. If that fails, repeat ICAL and reanalyze all samples since the last good CCV (DoD Box 59...if the lab chooses to demonstrate the success of routine corrective action through the use of 2 consecutive CCVs, then the concentrations of the two CCVs must be a two different levels within the original calibration curve with at least one falling below the middle of the calibration range.)	NA
Low-level calibration check standard (ICP only)	Daily, after one-point initial calibration	Within ± 20% of expected value	Correct problem, then reanalyze. No sample may be analyzed without a valid low-level calibration check standard. Low-level calibration check standard should be ≤ RL	NA
MB	One per prep batch	No analytes detected > ½ RL For common lab contaminants, no analytes > RL	Correct problem, then see criteria in box D-5; if required, reprep/reanalyze MB and all associated samples	Apply B-flag to all results for the contaminated analyte for all samples in the associated prep batch
Calibration Blank (ICB / CCB)	Before beginning a sample run, after every 10 samples, and at the end of the analysis sequence	No analytes detected > 2x MDL	Correct problem, then reprep and reanalyze calibration blank and previous 10 samples	Apply B-flag to all results for the contaminated analyte for all samples in the associated prep batch
Interference check solution (ICS) (ICP only)	At the beginning of analytical run	ICS-A: Absolute value of concentration for all non-spiked analytes < 2x MDL (unless they are verified trace impurity from one of the spiked analytes) ICS-AB: ± 20% of expected value	Terminate analysis; locate and correct problem; reanalyze ICS	NA
LCS (containing all analytes to be reported)	One LCS per prep batch	DoD specified QC criteria, if available	Correct problem, reprep/reanalyze the LCS and all samples in the associated prep batch for all failed analytes, if sufficient sample is available	Apply Q-flag to specific analyte(s) in all samples in the prep batch.

Table B-6 cont.				
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**
Dilution Test	Each prep batch or when a new or unusual matrix is encountered	5x dilution must agree within ± 10% of the original determination Note: Only applicable for samples with concentrations > 50x MDL (ICP) or > 25x MDL (GFAA and CVAA)	ICP: Perform post-digestion spike (PDS) GFAA: Perform recovery test CVAA: Perform matrix spike	NA
Post-digestion spike (PDS) (ICP only)	When dilution test fails or analyte concentration in all samples < 50 x MDL	Spike addition must produce a level between 10-100 x MDL. Recovery limit: 75-125% of expected value	Run samples by MSA or see flagging criteria	Apply J-flag to all associated sample results (for same matrix) for specific analyte(s)
Recovery Test (GFAA only)	When dilution test fails or analyte concentration in all samples < 25x MDL	Recovery limit: 85-115% of expected value	Run samples by MSA or see flagging criteria	Apply J-flag to all associated sample results (for same matrix) for which MSA was not run
MSA or Internal Standard Calibration	When matrix interference is suspected	NA	NA	NA Document in Case Narrative
MS	One per prep batch per matrix	For matrix evaluation, use DoD specified QC criteria for LCS	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample
MSD or Sample Duplicate	One per prep batch per matrix	RPD ≤ 20% (between MS and MSD or sample and sample duplicate)	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample
Results reported between LOD and LOQ			Apply J-flag to all results between LOD (MDL) and LOQ (RL)	

Notes:
1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

STL Chicago
STANDARD OPERATING PRACTICE (SOP) CHANGE FORM

Original SOP Number/Revision #: UME-6010B Rev 07 Last Mod ID (circle): NA/ A
SOP Title: Trace ICP Analysis; SW-846 Method 6010B
Affected SOP Section Number(s): Section 9.0
Effective Date: 06/02/06

CONTROLLED DISTRIBUTION

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Revision Number with Mod ID:

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. **Append this form to the front of the SOP copy.**

1. Reason for SOP Change: Addition of SiO2 and Hardness Calculations

2. Summary of Procedure Change (circle to indicate if there are attachments to this form: No / Yes: # pages attached = _)

Upon the next revision the SOP will be updated to include the calculations for SiO2 and Hardness (SM 2340B).

Calculation of SiO2:

(Si) Silicon Raw (mg/L) X 2.1392 X Prep Factor

Calculation of Magnesium Hardness:

(Mg) Magnesium Raw (mg/L) X 4.118 X Prep Factor

Calculation of Calcium Hardness:

(Ca) Calcium Raw (mg/L) X 2.497 X Prep Factor

Calculation of Total Hardness:

(((Ca) Calcium Raw (mg/L) X 2.497) + ((Mg) Magnesium Raw (mg/L) X 4.118)) X Prep Factor

Final units appropriate to reporting requirements

5/31/06
Initiated/Reviewed By: Name/Date

N/A
Initiated/Reviewed By: Name/Date

5/31/06
Approval Signature/Date: Section Manager

Teresa A. Preston 5/31/06
Approval Signature/Date: QA Manager or Designee

STL Chicago
STANDARD OPERATING PRACTICE (SOP) CHANGE FORM

Original SOP Number/Revision #: UME-6010B Rev 07 Last Mod ID (circle): NA (B)
SOP Title: Metals Analysis Trace Inductively Coupled Argon Plasma by SW-846 6010B
Affected SOP Section Number(s): New Section 8.1.6
Effective Date: October 23, 2006

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1. Reason for SOP Change: Update for Clarification for Frequency of Post Digestion Spikes

2. Summary of Procedure Change (circle to indicate if there are attachments to this form: (No) / Yes: # pages attached = _)

Section 8.1.6 will be created:

"If the serial dilution is not within limits, a Post Digestion spike may be analyzed to compensate for the matrix effect. Post Digestion spikes are analyzed on a project, program or client request basis. Recoveries must fall between 75-125%."

x Lisa M. Odusko 10/25/06
Initiated/Reviewed By: Name/Date

N/A
Initiated/Reviewed By: Name/Date

x Diane L. Hargis 10/23/06
Approval Signature/Date: Section Manager

Maureen D. Kinney 10-23-06
Approval Signature/Date: QA Manager or Designee

SOP No.	Revision No.	Date	Page
UME-6010B	07	01/13/06	1 of 27

TITLE: Metals Analysis Trace Inductively Coupled Argon Plasma by SW-846 6010B (Simultaneous Operation)

Updated by:	Signature:	Date:
Todd D. Smith Senior Analyst		1/9/06

Approved by:	Signature:	Date:
Jodi L. Gromala Supervisor, Metals Dept.		1/9/06
David W. Mazur Env. Health & Safety Coor.		1/10/06
Terese A. Preston Quality Manager	Terese A. Preston	1/10/06

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) outlines the guidelines for determining metal concentrations by Trace Inductively Coupled Argon Plasma (ICAP) Emission Spectrometry - Simultaneous Operation. This SOP was written using U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste", Third Edition, Method 6010B as a reference.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

Specific requirements pertaining to the DOD QSM Version 3.0 are located in Appendix A. These requirements are additionally applicable to all NFESC projects. Any deviations from these procedures and/or variances from must be addressed appropriately in accordance with standard operating protocol and pre-approved on a project by project basis.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Instrument Detection Limits

Instrument Detection Limits (IDLs) are performed on a quarterly basis for each element and for each instrument (as specified in CLP). These limits are used to gauge instrument sensitivity and when routinely evaluated, instrument performance without the introduction of method variance can be determined.

1.1.3 Reporting Limits

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values ~3-5x the respective MDL to ensure confidence in the value reported. Client specific requests for reporting to the

MDL are special circumstances not to be confused with the previous statement. Refer to Table 1 for element wavelength and reporting limits.

1.1.4 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.2 Summary of Method

ICAP is a technique for the analysis of soluble or digested samples for metal concentrations using atomic emission spectrometry. All matrices, including water, TCLP extracts, wastes, soils, sludges and sediments, require digestion prior to analysis. The instrument is capable of analyzing simultaneously 29 different elements on a sample.

2.0 INTERFERENCES

Spectral, Physical and Chemical Interferences are the three main interferences that are commonly present on the ICAP.

2.1 Spectral Interferences

Mainly caused by continuous background wavelength, stray light from a high concentration element or overlap of a spectral line from another element. The ICAP can correct for the first two types of interferences by using background correction adjacent to the wavelength. Spectral overlap can be corrected by monitoring the interfering wavelength and computer correcting the results for the false concentration. The values used to correct are known as Inter-Element Correction Factors or IEC's.

2.2 Physical Interferences

Usually associated with the sample uptake and nebulization processes. These interferences can usually be eliminated by using a peristaltic pump which assures a constant sample uptake rate. If a sample is extremely viscous or contains a very high dissolved solids concentration, a dilution of the sample may be required to assure a constant and smooth nebulization rate.

2.3 Chemical Interferences

Normally not significant on the ICAP. These interferences include ionization effects and molecular compound formation. Chemical interferences are highly dependent on the sample matrix type and the element.

Trace ICP can have some ionization effects caused by torch positioning. To eliminate these effects, Cesium is added to the internal standard solution (100 mLs / 1-Liter).
Most interferences can be corrected by ensuring a constant sample uptake rate and by using the correcting abilities of the computer. If severe interferences are suspected, an alternate method such as Graphite Furnace Atomic Absorption (GFAA) can be used or to verify the ICAP results.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

- The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.
- Parts of the instrument can be extremely hot. Care should be taken if the instrument needs to be adjusted internally.
- Proper ventilation is required due to sample fumes and extreme heat generation (RF generator and plasma) and plasma emissions. People with medical conditions that may respond to ozone emissions should exercise caution.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

4.1 Instrumentation

3 - Thermo Jarrell Ash ICAP 61E Trace Analyzer. These instruments are simultaneous ICAP's which currently have 31 analytical wavelengths. Additional wavelengths may be added as required.

The instruments are operated via desktop computers and Thermo Jarrell Ash software (Version 6.2). They also come equipped with a peristaltic pump for sample uptake and an autosampler.

4.2 Supplies

- Volumetric Flasks (Class A): 100 mLs; 200 mLs; 1000 mLs
- Eppendorf Pipettes, varying volumes

5.0 REAGENTS AND STANDARDS

5.1 Reagents

- Milli-Q Water
- *Concentrated Nitric Acid (HNO_3) - InstraPure
- *Concentrated Hydrochloric Acid (HCl) - InstraPure

*Purchased from a vendor.

5.2 Standards and QC Solutions

All stock standards and QC solutions are purchased from an outside supplier in aqueous form. Two types of standards are used: single element and custom mixed standards. Single element standards are available for most elements at a 1,000 mg/L concentration. The shelf life of all purchased solutions are as stated by the manufacturer and are listed in LabNet (LIMS).

5.2.1 Calibration Standards

Prepared with Milli-Q water that has been acidified with 1% HNO_3 and 5% HCl. The calibration standards are prepared daily as follows:

A. Calibration Blank

Add ~500 mLs of Milli-Q water to a 1-L Class A volumetric flask. Repipette 10 mLs conc. HNO_3 and 50 mLs conc. HCl into the flask. Dilute to volume with Milli-Q water and mix thoroughly.

B. Calibration Standards (Refer to Attachment 1 for element concentrations)

Standard	Preparation
S1	• Add ~50 mLs of Milli-Q water to a 200 mL Class A volumetric flask. • Re-pipette 2 mLs conc. HNO_3 into the flask. • Re-pipette 10 mLs conc. HCl into the flask. • Using Eppendorf pipettes, add 2.0 mLs each of: RFW-ICPT-STD-1B RFW-ICPT-STD-1C RFW-ICPT-STD-1D • Dilute to volume with Milli-Q water and mix thoroughly.
S1A	• Add ~50 mLs of Milli-Q water to a 200 mL Class A volumetric flask. • Re-pipette 2 mLs conc. HNO_3 into the flask. • Re-pipette 10 mLs conc. HCl into the flask. • Using Eppendorf pipettes, add 0.8 mLs each of: RFW-ICPT-STD-1B RFW-ICPT-STD-1C RFW-ICPT-STD-1D • Dilute to volume with Milli-Q water and mix thoroughly.
S1B	• Add ~50 mLs of Milli-Q water to a 200 mL Class A volumetric flask. • Re-pipette 2 mLs conc. HNO_3 into the flask. • Re-pipette 10 mLs conc. HCl into the flask. • Using Eppendorf pipettes, add 1.0 mLs each of RFW-ICPT-STD-1B RFW-ICPT-STD-1C RFW-ICPT-STD-1D • Dilute to volume with Milli-Q water and mix thoroughly.
S2	• Add ~50 mLs of Milli-Q water to a 200 mL Class A volumetric flask. • Re-pipette 2 mLs conc. HNO_3 into the flask. • Re-pipette 10 mLs conc. HCl into the flask. • Using Eppendorf pipettes, add 2.0 mLs each of: RFW-ICPT-STD-2A RFW-ICPT-STD-2B RFW-ICPT-STD-3 • Dilute to volume with Milli-Q water and mix thoroughly.

Standard	Preparation
S2A	• Add ~50 mLs of Milli-Q water to a 200 mL Class A volumetric flask. • Re-pipette 2 mLs conc. HNO_3 into the flask. • Re-pipette 10 mLs conc. HCl into the flask. • Using Eppendorf pipettes, add 0.8 mLs each of: RFW-ICPT-STD-2A RFW-ICPT-STD-2B RFW-ICPT-STD-3. • Dilute to volume with Milli-Q water and mix thoroughly.
S2B	• Add ~50 mLs of Milli-Q water to a 200 mL Class A volumetric flask. • Re-pipette 2 mLs conc. HNO_3 into the flask. • Re-pipette 10 mLs conc. HCl into the flask. • Using Eppendorf pipettes, add 1.0 mL each of: RFW-ICPT-STD-2A RFW-ICPT-STD-2B RFW-ICPT-STD-3 • Dilute to volume with Milli-Q water and mix thoroughly.

5.2.2 QC Solutions (Refer to Attachment 2 for element concentrations.)

Prepared with Milli-Q water that has been acidified with 1% HNO_3 and 5% HCl. All QC Solutions are recorded in the intermediate standard traceability logbook.

QC Solution	Preparation (In a 1-L Class A volumetric flask filled w/ ~500 mLs of Milli-Q water, add the following for each QC Solution):
Initial Calibration Verification (ICV)	• 10 mLs conc. HNO_3 • 50 mLs conc. HCl. • 8 mLs of CCV Soln. A • 8 mLs of CCV Soln. A1 • 8 mLs CCV Soln. B • 1.84 mLs of 10,000 ug/mL Ca • 1.6 mLs of 10,000 ug/mL Na, Fe • 1.68 mLs of 10,000 ug/mL Mg • 3.6 mLs of 10,000 ug/mL K, Al • Dilute to volume with Milli-Q water and mix thoroughly.
Continuing Calibration Verification (CCV)	• 10 mLs conc. HNO_3 • 50 mLs conc. HCl. • 10 mLs of CCV Soln. A • 10 mLs of CCV Soln. A1 • 10 mLs of CCV Soln. B • 2.3 mLs of 10,000 ug/mL Ca • 2.0 mLs of 10,000 ug/mL Na, Fe • 2.1 mLs of 10,000 ug/mL Mg • 4.5 mLs of 10,000 ug/mL K, Al • Dilute to volume with Milli-Q water and mix thoroughly.

QC Solution	Preparation (In a 1-L Class A volumetric flask filled w/ ~500 mLs of Milli-Q water, add the following for each QC Solution):
CRI [Contract Required Detection Limit (CRDL) Standard for ICAP]	• 10 mLs conc. HNO_3 • 50 mLs conc. HCl • 40 uLs of Cd Intermediate Std.* • 80 uLs of Be Intermediate Std. * • 10 uLs of 10,000 ug/mL Fe • 10 uLs of 1,000 ug/mL Co, Se, Ag, Sr, Ti, V, Pb • 20 uLs of 10,000 ug/mL Ca, Mg • 20 uLs of 1,000 ug/mL As, Cu, Cr, Mn, Ni, Ba, Mo, Tl, Zn • 40 uLs of 10,000 ug/mL Al • 40 uLs of 1,000 ug/mL Sb, Sn • 200 uLs of 10,000 ug/mL Na • 100 uLs of 10,000 ug/mL K • 100 uLs of 1,000 ug/mL B, Bi • 400 uLs of 1,000 ug/mL Si • Dilute to volume with Mill-Q water and mix thoroughly. * Cd Intermediate = 1:10 dilution of 1,000 ppm Cd. * Be Intermediate = 1:10 dilution of 1,000 ppm Be
Interferent Check Standard (ICSA)	• 10 mLs conc. HNO_3 • 50 mLs conc. HCl • 100 mLs of CLP Interferent A Solution • Dilute to volume with Milli-Q water and mix thoroughly
Interferent Check Standard (ICSAB)	• 10 mLs conc. HNO_3 • 50 mLs conc. HCl • 100 mLs of CLP Interferent A Solution • 10 mLs of CLPP-ICS-B4 • Dilute to volume with Milli-Q water and mix thoroughly.

6.0 CALIBRATION (NON-DAILY)

6.1 Linear Range Analysis Standard (LRS)

LRS calibration is performed quarterly that covers the anticipated range of measurement. The expected recovery limit for this verification standard is 95-105%. This is used to verify linearity and document the upper limit of the calibration range for each element. At least one of the calibration standards will be at or near the reporting limit. The calibration curve generated must have a correlation coefficient of $\geq$ 0.995 in order to consider the responses linear over that range. All samples found to be above the ICAP linear range are diluted and re-analyzed until the concentration falls within the instruments linear range.

6.2 Inter-Element Correction (IEC)

Correction factors for spectral interference due to Al, Ca, Fe, and Mg will be determined at least annually for all wavelengths used for each analyte reported or any time the ICAP is adjusted in any way that may affect the IECs. Correction factors for spectral interferences other than Al, Ca, Fe, and Mg are recommended and are performed as needed and documented with the instrument records.

7.0 PROCEDURE

7.1 Quality Control Checks

The following section summarize the quality control (QC) samples associated with ICAP analysis.

QC Sample	Frequency	Control Limit [1]
Method Blank (MB)	1 per 20 samples	≤ Reporting Limit
Lab Control Sample (LCS) [2]	1 per 20 samples	80 – 120 %
Matrix Spike (MS) [3,6]	1 per 20 samples	75 – 125 %
MS Duplicate (MSD) [3,6]	1 per 20 samples	75 – 125 %; 20 RPD
Duplicates (MD) [4,6]	1 per 20 samples	20 RPD
Serial Dilution (5x) [5]	1 per 20 samples	± 10% of the original result

[1] Refer to Section 8 for additional details.
[2] LCS Duplicate (LCD) is performed only when required by the client or project.
[3] If sample concentration is ≤ 4X spike level, 75-125%; if sample concentration is > 4X spike level, no control range. If TCLP matrix spike is < 50%, Standard Addition must be performed.
[4] If ≥ 5X reporting limit, 20 RPD; if < 5X reporting limit ± reporting limit; if < reporting limit no control range.
[5] If the analyte concentration is >10X the MDL, results should agree within ±10% of the original sample result.
[6] The sample selection for matrix QC, if not specified by the client or on the chain-of-custody, is rotated among client samples so that various matrix problems may be noted and/or addressed...pre-determined by the digestion department.

7.2 Sample Preservation and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Holding Time[1]	Preservation	Reference
Waters	180 days	HNO_3, pH < 2; Cool 4 ± 2°C	40 CFR Part 136.3
Soils	180 days	Cool 4 ± 2°C	N/A

[1] Inclusive of digestion and analysis.

7.3 Sample Preparation

The most commonly used digestion procedures are SW-846 Methods 3010A (waters) and 3050B (soils). Refer to USP-3000 for details on sample digestion. The samples are received in the metals laboratory as 25, 50 or 100 mL final volumes.

7.4 Calibration / Standardization

7.4.1 Instrument Set Up

Set up the instrument with the proper operating conditions as defined in the TJA instrument manual. The instrument must be allowed to become thermally stable (~1-hour) prior to profiling and calibration. The instrument is profiled using a 1-ppm Arsenic standard (S1) by aspiration and selecting the automatic profile feature from the TJA software. The peak position reading should be within +/- 0.1. If the reading is acceptable, record the peak area in the logbook & rinse. If the reading is > +/- 0.1, set the micrometer to the adjusted vernier position given by the instrument and profile again to verify. Record the peak area in the logbook and rinse. The instrument is now ready to calibrate.

7.4.2 Standardization

Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. All sample measurements must be made within the linear range of the instrument.

The instrument is standardized using a calibration blank and 3 calibration standards, which consist of 6 multi-element solutions. The results are given in intensities. Minimum requirement is a blank and a standard.

Standard	Frequency	Control Limit
Calibration Curve	Initially	Corr. Coeff. ≥ 0.995
High Standards (S1, S2)	After the Calibration Curve	± 5% of the Known Conc.
Initial Cal. Verif. (ICV)	After the Calibration Curve	± 10% of the Known Conc.
Initial. Cal. Blank (ICB)	After the ICV	≤ Reporting Limit
CRI	Daily, every 8 hrs. thereafter	None Required
ICSA / ICSB	Daily, every 8 hrs. thereafter	± 20% of the Known Conc.
Cont. Cal. Verif. (CCV)	Every 10 reading; End of each run	± 10% of the Known Conc.
Cont. Cal. Blank (CCB)	Every 10 readings; End of each run	≤ Reporting Limit

7.5 Preventive Maintenance

The required preventive maintenance is listed in the preventive maintenance logbooks which are kept at the instruments. All maintenance is recorded in these logbooks along with the date and the signature of the analyst performing the maintenance. The instruments are under a full service contract with the manufacturer for all major repairs.

7.5.1 Daily Maintenance

Includes changing the pump tubing for consistent sample uptake and a visible check of the waste container to make sure that it doesn't overflow.

7.5.2 Weekly Maintenance

Includes checking the air filters on the back of the instrument for excessive dust buildup, and checking the tip of the torch for excessive buildup of material.

7.5.3 Monthly Maintenance

Includes cleaning and checking the water re-circulator for proper fluid level, cleaning the spray chamber.

7.6 Sample Analysis

7.6.1 Analytical Run

After the instrument is standardized (Section 7.4.2), an analytical run is initiated. The first run of the day would proceed as follows:

- S1,S2 Reanalysis of calibration standard as a sample
- ICV Initial Calibration Verification
- ICB Initial Calibration Blank
- CRI Spiked Blank Sample
- ICSA Interferent Check Standard A
- ICSB Interferent Check Standard B
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank
- MB (1) Method Blank
- LCS (2) Laboratory Control Sample
- Sample (3)
- Sample (4) Serial Dilution (L)
- Sample (5) Matrix Duplicate (MD)
- Sample (6) Matrix Spike (MS)
- Sample (7) Matrix Spike Duplicate (MSD)

- Sample (8)
- .
- Sample X (10)
- CCV Continuing Calibration Verification
- CCB Continuing Calibration Blank

If the CCV and CCB results are acceptable, the run may continue without restandardization. If any of the post-run QC is out of control, or close to being out of control, the instrument is restandardized before analyzing the next batch. Any samples with elements associated with an out of control CCV or CCB will be reanalyzed.

7.7 Documentation

7.7.1 Instrument Run-Log

The analysis of samples and standards is documented within the instrument run log (Attachment C), which must be for each days analysis, and is supported by the instrument print-out.

7.7.2 Traceability of Standards

Custom made and single element stock standard solution which are traceable to NIST or EPA are purchased. Upon receipt, each standard is entered into LabNet and is issued a unique source ID#. The manufacturer, lot #, date received, expiration date, date of verification and the initials of the recording analyst are also entered.

7.7.3 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews according to the criteria established on the data review checklist (Attachment D). Upon the first 100% review, the checklist is initialed and dated as reviewed. The package, with its review sheet, comments and any Corrective Action Reports (CARs) are submitted to the supervisor or peer reviewer for a second review. Once again, the checklist is initialed and dated by the second reviewer. The completed data review form remains on file with the original data.

8.0 QUALITY CONTROL

8.1 QC Summary

NOTE: The following laboratory acceptance criteria are set at default control limits. Statistical limits are generated on an annual basis from cumulative LCS data and can be implemented when specified by the client, contract, or QAP.

8.1.1 Method Blank (MB)

At least one MB and one LCS will be included in each digestion batch of 20 samples. Regardless of the matrix being processed, the LCS and MB will be in an aqueous media. The MBs are analyzed to determine if contaminants are being introduced into the sample via the sample preparation procedures.

8.1.2 Laboratory Control Sample (LCS)

The LCS is analyzed to determine the accuracy of the digestion process.

Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be within ±20% of the known concentration. If the LCS results are outside these control limits, all samples in the preparation set must be redigested and reanalyzed. Refer to Attachment E for element concentrations.

8.1.3 Matrix Duplicate (MD)

A duplicate sample will be prepared at a frequency of 5% (1 in 20 samples). A 20 RPD is set as the acceptance limits.

8.1.4 Matrix Spike (MS) / Matrix Spike Duplicate (MSD)

The MS / MSD will be prepared at a frequency of 5% (1 in 20 samples). The recovery must be within 75–125%. (Exception allowed if the sample concentration exceeds 4 times the spike added concentration.)

TCLP - If the MS recovery is <50% and the concentration does not exceed the regulatory limit or the sample concentration is within 20% of the regulation level, the Method of Standard Addition (MSA) is required. Three aliquots of the sample are spiked at 50%, 100% and 150% of the sample concentration or, if the sample concentration is < RL, the MSA is at 50%, 100% and 150% of the MS level. The data is subjected to linear regression whereas the concentration of the unknown is the. x-intercept and the correlation coefficient value must be ≥ 0.995.

8.1.5 Serial Dilution

A Serial Dilution (5X) will be prepared from the digestate at a frequency of 5% (1 in 20 samples). If the concentration is >50 times the MDL, results should agree within +/- 10% of the original results.

8.2 Corrective Action

When an out-of-control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out-of-control situation may be caused by more than one variable. The analyst should seek the assistance of his/her supervisor, QA personnel, or other experienced staff if he/she are uncertain of the cause of the out-of-control situation. The analysis must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out-of-control situation should be reanalyzed. Out-of-control data must never be released without approval of the supervisor, or QA personnel.

The following steps that must be taken when an out-of-control situation occurs:

- demonstrate that all the problems creating the out-of-control situation were addressed;
- document the problem and the action which was taken to correct the problem on a CAR;
- document on the CAR that an in-control has been achieved; and
- receive approval (signature) of the supervisor or QA personnel prior to the release of any analytical data associated with the problem.

QC Indicator	Suggested Corrective Actions
Calibration Curve	• reanalyze the standard curve; • prepare a new stock and/or working standards; • check the reagents/solutions and prepare fresh if necessary.
ICV	• repeat the ICV to verify proper preparation; • prepare a new ICV from original stock; • recalibrate with a new standard curve; • prepare a new stock and/or working standards; • check the reagents/solutions and prepare fresh if necessary.
ICB	• prepare a new ICB to verify proper preparation; • verify that the instrument base-line is stable and perform necessary maintenance, cleaning, etc.. to achieve stability; • determine the source of contamination by process of elimination, carryover from a previous analysis or reagent contamination and correct the problem; • check the reagents/solutions and prepare fresh if necessary; • correct for any contamination and reanalyze the ICB and any associated samples.

QC Indicator	Suggested Corrective Actions
LCS	<u>If the LCS is low:</u> • reanalyze the LCS and all samples in the set for the failed analyte(s) to confirm that it is out of control. • If continued out of control, redigest and reanalyze the set. • Write a CAR. <u>If the LCS is high:</u> • reanalyze the LCS and all samples in the set for the failed analyte(s) to confirm that it is out of control. • check for contamination of reagents, LCS stock solution, or in the preparation area; • correct for contamination, redigest and re-analyze the set; • Write a CAR.
MB	• reanalyze the MB to verify that it is beyond the reporting limit; • determine the source of contamination; • determine if a high value is due to contamination; • check for contamination of reagents or in the preparation area; • correct for contamination, reanalyze the set; • in the extreme case where all samples in the set are at least 10x > the MB or < RL, reanalysis will not be required; however, a CAR will be written and approved by the supervisor or section manager.
MD	• a CAR will be written and approved by the supervisor or section manager.
MS / MSD	• a CAR will be written and approved by the supervisor or section manager.
Serial Dilution (L)	• prepare a new serial dilution to verify proper preparation; • a CAR will be written and approved by the supervisor or section manager.
CCV	• repeat the CCV to verify proper preparation; • prepare a new CCV from the original stock; • check for instrument base-line drift or a change in one or more of the reagents; • check the reagents/solutions and prepare fresh if necessary; • recalibrate with a new standard curve and repeat all samples since the previous in control CCV; • never dispose of any samples until you are sure that all QC are within the control limits.
CCB	• check reagents/solutions to verify proper preparation and prepare fresh if necessary; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc., to achieve stability; • correct for any contamination (carryover from a previous analysis or reagent contamination) and reanalyze the CCB and any associated samples; • never dispose of any samples until you are sure that all QC are within the control limits.

QC Indicator	Suggested Corrective Actions
Additional CAs	• If any of the ICV, ICB, ISA, ISB, CCV or CCB results are out-of-control for any element, the instrument is restandardized and the samples associated with the out-of-control elements are reanalyzed. • If the MB or LCS are out of control for any element, the samples are redigested. An exception is if the sample concentrations are ≥ 10X the MB contamination or < RL. In this case, the results are reported as is. • If any of the MD or MS/MSD results are out of control, the client is notified of the poor results via a case narrative that is sent with the data report. • CARs are completed by the analyst performing the analysis. The forms are then reviewed and signed by the supervisor or section manager. The signed forms are filed with the original data and a copy is kept on file in the Metals Department.

9.0 DATA ANALYSIS AND CALCULATIONS

The sample results are stored in a data file on the desktop computer. The data is transferred over to LabNet and edited there. This system helps to eliminate transcription errors, since data is not entered by hand.

9.1 Accuracy

9.1.1 ICV / CCV, LCS % Recovery = $\frac{\text{observed concentration}}{\text{known concentration}} \times 100$

9.1.2 MS / MSD % Recovery = $\frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$

9.2 Precision (RPD)

9.2.1 Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

9.3 Concentration

$$\text{mg/kg or L} = \frac{C \times V \times D}{W}$$

Where:
C = sample concentration in extract (ppm)
V = Volume of extract (mL)
D = Dilution Factor
W = Weight/Volume of sample aliquot extracted (grams or mLs)

NOTE: All dry weight corrections are made in LabNet at the time the final report is prepared.

10.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Waste from this procedure will enter the "Corrosive Wastewater" wastestream.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1.0, 7.0 and 8.0.

12.0 REFERENCES

Refer to Section 1.0.

13.0 ATTACHMENTS

Table 1. Element and Reporting Limits
Attachment 1. Standard Stock Solutions
Attachment 2. Stock QC Solutions
Attachment 3. Example: Analysis Run Log / Maintenance Log
Attachment 4. Example: Data Review Form
Attachment 5. Known Digested Quality Control

Appendix A: Requirements for DOD QSM Version 3.0 – Table B-1 and Table B-6

Historical File:

Revision 00: 02/11/98
Revision 01: 01/29/99
Revision 02: 03/20/00
Revision 03: 06/29/01
Revision 04: 09/13/02
Revision 05: 10/30/03
Revision 06: 01/03/05
Revision 07: 01/09/06

Reasons for Revision; Revision 07:

- Annual Review – Remove reference to ICP3 in Table 1
- Section 1: Add language specific to the DoD QSM requirements
- Add Appendix A: DoD QSM Requirements Summary Tables

Table 1.

Element and Reporting Limits

Element	ICAP 61E (ICP4) Wavelength (nm)	ICAP 61E (ICP5) Wavelength (nm)	Reporting Limits[1] Waters (mg/L)	Soils (mg/kg)
Al	308.2	308.2	0.2	20
Sb	206.8	206.8	0.02	2
As	189.0	189.0	0.01	1
Ba	493.4	493.4	0.01	1
Be	313.0	313.0	0.004	0.4
Bi	223.0	N/A	0.05	5
B	249.6	249.6	0.05	5
Ca	317.9	317.9	0.1	10
Cd	226.5	226.5	0.002	0.2
Cr	267.7	267.7	0.01	1
Co	228.6	228.6	0.005	0.5
Cu	324.7	324.7	0.01	1
Fe	271.4	271.4	0.10	10
Pb	220.3	220.3	0.005	0.5
Mg	279.0	279.0	0.1	10
Mn	257.6	257.6	0.01	1.0
Mo	202.0	202.0	0.01	1
Ni	231.6	231.6	0.01	1
K	766.4 / 404.7	766.4	0.5 / 10	50 / 1,000
Se	196.0	196.0	0.01	1
Si	288.1	288.1	0.2	20
Ag	328.0	328.0	0.005	0.5
Na	330.2	330.2 / 588.9	1	100
Sr	NA	421.5	0.005	0.5
Tl	190.8	190.8	0.01	1
Sn	189.9	189.9	0.02	2
Ti	337.2	334.9	0.005	0.5
V	292.4	292.4	0.005	0.5
Y[2]	371.0	371.0	N/A	N/A
Zn	206.2	206.2	0.02	2

[1]These are routine Trace ICAP reporting limits (RL). Lower RLs are available and can be used per client request. RLs will vary depending on sample size/volume, dilution factors, dry weight reporting for soils, and changes in MDLs.
[2]Y is used as an internal standard and is introduced continuously to all samples (including standards and QC samples) via the peristaltic pump at an approximate concentration of 5 ppm.

Attachment 1.

Standard Stock Solutions

Vendor	Stock Name	Element	Conc. (mg/L)	S1A	S1B	S1	S2A	S2B	S2
Inorganic Ventures	RFW-ICPT-STD-1B	Sb	100	0.4	0.5	1			
		Mo	100	0.4	0.5	1			
		Si	100	0.4	0.5	1			
		Sn	100	0.4	0.5	1			
		Ti	100	0.4	0.5	1			
Inorganic Ventures	RFW-ICPT-STD-1C	Al	1,000	4	5	10			
		Fe	1,000	4	5	10			
		K	1,000	4	5	10			
		Na	1,000	4	5	10			
		Li	800	2	4	8			
		Mg	800	2	4	8			
		Ca	400	1.6	2	4			
Inorganic Ventures	RFW-ICPT-STD-1D	As	100	0.4	0.5	1			
		Ba	100	0.4	0.5	1			
		Be	100	0.4	0.5	1			
		Bi	100	0.4	0.5	1			
		B	100	0.4	0.5	1			
		Cd	100	0.4	0.5	1			
		Cr	100	0.4	0.5	1			
		Cu	100	0.4	0.5	1			
		Pb	100	0.4	0.5	1			
		Ni	100	0.4	0.5	1			
		Se	100	0.4	0.5	1			
		Ag	100	0.4	0.5	1			
		Sr	100	0.4	0.5	1			
		Tl	100	0.4	0.5	1			
		Zn	100	0.4	0.5	1			
Inorganic Ventures	RFW-ICPT-STD-2A	Al	10,000				40	50	100
		K	10,000				40	50	100
Inorganic Ventures	RFW-ICPT-STD-2B	Ca	5,000				20	25	50
		Fe	5,000				20	25	50
		Mg	5,000				20	25	50
		Na	5,000				20	25	50
Inorganic Ventures	RFW-ICPT-STD-3	Pb	2,000				8	10	20
		Mn	1,000				4	5	10
		V	1,000				4	5	10

Attachment 2.

Example of Stock QC Solutions

Vendor	Stock Name	Element	Conc. (mg/L)	ICV (mg/L)	CCV (mg/L)
High Purity	CCV Solution A	As	50	0.4	0.5
		B	50	0.4	0.5
		Ba	50	0.4	0.5
		Be	50	0.4	0.5
		Bi	50	0.4	0.5
		Cd	50	0.4	0.5
		Co	50	0.4	0.5
		Cr	50	0.4	0.5
		Cu	50	0.4	0.5
		Ni	50	0.4	0.5
		Pb	50	0.4	0.5
		Se	50	0.4	0.5
		Fe	500	20	25
		Mn	500	4	5
		V	500	4	5
		Tl	50	0.4	0.5
		Zn	50	0.4	0.5
		Sr	50	0.4	0.5
High Purity	CCV Solution A2	Ca	200	20	25
		Li	400	---	---
		Na	500	20	25
		Al	500	40	50
		Mg	400	20	25
		K	500	40	50
High Purity	CCV Solution B	Ag	50	0.4	0.5
		Sb	50	0.4	0.5
		Mo	50	0.4	0.5
		Si	50	0.4	0.5
		Sn	50	0.4	0.5
		Ti	50	0.4	0.5
Ultra	Single Elements * spiked on top of custom mixes.	Al	10,000	40	50
		Ca	10,000	20	25
		Fe	10,000	20	25
		Na	10,000	20	25
		K	10,000	40	50
		Mg	10,000	20	25

Attachment 2.
(continued)
Examples of Stock QC Solutions

Vendor	Stock Name	Element	Conc. (mg/L)	CRI Conc. (mg/L)
Inorganic Ventures	Beryllium	Be	1,000	0.008
	Chromium	Cr	1,000	0.02
	Cobalt	Co	1,000	0.01
	Copper	Cu	1,000	0.02
	Manganese	Mn	1,000	0.02
	Nickel	Ni	1,000	0.02
	Silver	Ag	1,000	0.01
	Vanadium	V	1,000	0.01
	Zinc	Zn	1,000	0.02
	Antimony	Sb	1,000	0.04
	Arsenic	As	1,000	0.02
	Cadmium	Cd	1,000	0.004
	Lead	Pb	1,000	0.01
	Selenium	Se	1,000	0.01
	Thallium	Tl	1,000	0.02
Inorganic Ventures	Calcium	Ca	10,000	0.2
	Potassium	K	10,000	1.0
	Magnesium	Mg	10,000	0.2
	Sodium	Na	10,000	2.0
	Iron	Fe	10,000	0.1
	Aluminum	Al	10,000	0.04
	Barium	Ba	1,000	0.02
	Boron	B	1,000	0.1
	Bismuth	Bi	1,000	0.1
	Molybdenum	Mo	1,000	0.02
	Silicon	Si	1,000	0.4
	Tin	Sn	1,000	0.04
	Strontium	Sr	1,000	0.01
	Titanium	Ti	1,000	0.01

Attachment 2.
(continued)
Stock QC Solutions

Vendor	Stock Name	Element	Conc. (mg/L)	ICSA Conc. (mg/L)
Inorganic Ventures	CLP Interferents "A" Solution	Al	5,000	500
		Ca	5,000	500
		Mg	5,000	500
		Fe	2,000	200
				ICSB Conc. (mg/L)
Inorganic Ventures	CLP Interferent A Solution	Al	5,000	500
		Ca	5,000	500
		Mg	5,000	500
		Fe	2,000	200
Inorganic Ventures	CLPP-ICS-B4	Cd	100	1
		Ni	100	1
		Zn	100	1
		Sb	60	0.6
		Ba	50	0.5
		Be	50	0.5
		Co	50	0.5
		Cr	50	0.5
		Cu	50	0.5
		Mn	50	0.5
		V	50	0.5
		Ag	20	0.2
		As, Tl	10	0.1
		Pb, Se	5	0.05

Attachment 3.

Example: Analysis Runlog / Maintenance Log

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TJA Trace ICAP (61E) Analysis Log – ICP5 Page No._____

Date	Initials	File Name	Dig. Set	Int. Std	Sample Nos.	Parameters	Comments
				As = Y =			
				As = Y =			
				As = Y =			
				As = Y =			
				As = Y =			
				As = Y =			
				As = Y =			
				As = Y =			
				As = Y =			

Reviewed by:_____ Date:_____ CHI-22-14-062/A/11/01

STL Chicago
TJA Trace ICAP (61E) – ICP5
Instrument Maintenance Log

Page No._____

	Date/Initials	Date/Initials	Date/Initials	Date/Iniitals	Date/Initials	Date/Initials	Date/Initials
Daily Maintenance:							
Check/Change Pump Tubing							
Check Waste Container							
Weekly Maintenance:							
Clean Air Filters							
Check Torch for buildup (Note Cleaning)							
Check/Change Printer Ribbon							
Monthly Maintenance:							
Check/Refill Recirculator							
Check Nebulizer/Spray Chamber							

Comments:_____

_____

_____

_____

_____

Any Maintenance/Repair/Part Replacement performed that is not listed above must be documented in the Comments sections

Reviewer Signature:_____ Date:_____

Attachment 4.

Example: Data Review Checklist

STL Chicago
INORGANIC CLP / LEVEL IV DATA REVIEW CHECKLIST

Site Name: _____ Primary Reviewer: _____ Review Date: _____
JOB Number: _____ Secondary Reviewer: _____ Review Date: _____
No. of Samples/Matrix: a) WATER _____ b) SOIL _____ c) TCLP / SPLP _____ d) OTHER _____

Metals List: a) TAL b) PP c) TCLP d) Other (_____)
Report Level: **IDL** = a) CLP b) Non-CLP c) MDL d) Other **CRDL** = a) CLP b) Client c) Default RL d) Other

TASK : CAR's _____	PRI REV	SEC REV	COMMENTS
LAB CHRON: 1) Matches COC			
2) Proper Prep Links: S-F6 (Routine) S-F9 (TCLP/SPLP)			
3) Sample Hold Times Met			
Cyanide Reported on Forms	Y / N		Method: a) CLP b) SW846 9010B/9014
Initial / Continuing Calibration Criteria Met (CRA/CRI requirements met if applicable)			
FORM 1: Matches Report LabNet Report Units / Test Matrix Match Form 1's Dilutions due to interference's resulted in elevated RL's			
FORM 3: Method Blanks < CRDL			
FORM 5A: MS Recoveries Acceptable Default Limits _____ Statistical Limits _____ Project Limits _____ (S-F10 used to Clone By Project)			N
FORM 5B: PDS Performed			
FORM 6: Duplicate RPD Acceptable Default Limits _____ Statistical Limits _____ Project Limits _____ (S-F10 used to Clone By Project)			*
FORM 7: LCS Recoveries Acceptable Default Limits _____ Statistical Limits _____ Project Limits _____ (S-F10 used to Clone By Project)			^
FORM 8: MSA Analysis Performed			S
GFAA – Analytical Spike (AS) Recoveries Acceptable			W
GFAA – Repeat Analytical Recovery <40%			E
GFAA – Duplicate Injection Precision Met			M
FORM 9: Serial Dilution (SD) Acceptable			E
FORM 14's Correct			
RAW DATA: Complete (Match Batches to LabChron) a) Instr. Raw Data clearly displays the LabNet Batch number and includes the "Batch Worksheet" Report b) Prep Raw Data displays the LabNet Batch Number and includes the "Batch Worksheet" Report or "Raw Data" Report			

Comments on Reverse

TASK : CAR's _____	PRI REV	SEC REV	COMMENTS
LabNet Batch Status Report Displays Data At RVWD Status			
Incomplete JOB Status Report reveals no Outstanding Data			
NARRATIVE: 1) Holding Times			
2) Method References			Method: a) CLP b) SW846 c) Other
3) % Recoveries / RPD's			
4) Analytical Difficulties/Typos			

COMMENTS:

QC CYCLE	REASON
1	
2	

STL Chicago
ICAP Metals Data Review Checklist

Instrument ID: ICP 3 ICP 4 ICP 5 **Filename:**_____

Analyst Initial(s):_____ **LabNet Batch No.:**_____

Copies:

QC Type: a. CLP b. Standard c. TCLP d. Drinking Waters e. Solubles

I. Calibration:

Analyst	Reviewer	
		1. Verification of standard traceability and expiration (daily).
		2. Calibration is clearly documented:
		a. Instrument is calibrated using a Blank and three Calibration Standards. The correlation coefficient must be >0.995.
		b. Reanalysis of the top calibration standard as a sample. Control limits are 95 - 105%. (Run once daily prior to sample analysis).
		3. Calibration Verification: (10% Frequency):
		a. ICV/CCV: **Std./CLP** – Recovery 90-110% **EPA 200.7 (ICV)** – Recovery 95-105%
		b. ICB/CCB: **Std. QC:** < RL; **CLP QC:** < CRDL; **SW-846 QC:** < 3x MDL. (custom criteria code)
		4. **CLP QC:** An Initial & Final for each sample analysis run:
		a. CRI - 2x RL; No Limit Set
		b. ISA/ISAB - 80-120% Recovery
		5. **Std. QC:** Analyzed at the beginning of the day and every 8 hours thereafter:
		a. CRI: 2x CRDL; No Limit Set
		b. ISA/ISAB: 80-120% Recovery
		Refer to Run #:

Note: **CLP QC** requires the use of the IDL for calculating % Recoveries and Reporting Limits.
Standard QC requires the use of the RL for calculating % Recoveries and Reporting Limits.

II. Sample Analysis:

Analyst	Reviewer	
		1. Each Prep Batch consists of a maximum of 20 samples of a similar matrix:
		a. Prep Batches must be clearly identified
		b. 1 Prep Blank **CLP** - < CRDL; **Std. QC** - < RL **TCLP** - < TCLP Reporting Limit
		c. 1 LCS **Std./CLP** - 80-120% Rec.; **EPA 200.7** - 85-115% Rec.
		d. 1 Duplicate **Std.** - RPD or RSD limits are 20%; ***Unless*** the sample conc. is <5x RL then ± RL applies; for CLP ± CRDL applies. **EPA 200.7** - 10% Frequency
		e. 1 Matrix Spike **Std./CLP** - 75-125% Rec.; ***Unless*** the sample conc. exceeds the spike conc. by 4x; **EPA 200.7** - 70-130% Rec.; 10% Frequency
		f. Analytical MS **TCLP** - >50% (MSA performed if <50% recovery)
		g. Serial Dilution 1 per 20 samples; 10% Difference Limit
		h. A post-digestion spike (PMS) must be performed for CLP (75-125%) and 200.7 (85-115%) if the above limits are not met, (CLP - except for Ag, Na, Ca, K, and Mg for waters and soils, and Al and Fe for soils only).
		i. Turbidity Checked: **EPA 200.7 Drinking Water** (< 1 NTU; no prep required).

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ICAP Metals Data Review Checklist

II. Sample Analysis (continued):

Analyst	Reviewer	
		2. A Corrective Action Report (CAR) must be written for any out of control situations, clearly stating the problem and action to be taken:
		a. CAR included with original data run
		b. CAR with corrective action results included with the corrective action run.

III. Data Documentation

Analyst	Reviewer	
		1. Raw Data:
		a. Unused data is clearly identified.
		b. All crossed out data is initialed and dated.
		c. Out of control QC is clearly identified.
		d. Any data that has a tick (S, I, H or L) is commented on with appropriate action taken.
		e. The first page of the run must have the filename; instrument; and analyst's signature
		2. Run Log:
		a. Unused data is clearly identified.
		b. All cross outs are initialed and dated.
		c. Analyst's Signature is required.
		3. LabNet:
		a. Worksheet and data pages are printed.
		b. Unused data is clearly identified.
		c. All cross-outs are initialed and dated.
		d. First page must have the filename, instrument identification; analyst signature.
		e. Samples needing copying are clearly marked.
		f. Label Sample ID with the LabNet Batch their in.

III. Miscellaneous

Analyst	Reviewer	
		1. Is Sample Prep Linked?
		2. Is TCLP Linked? (Shift F9 from the start page)
		3. Did all dilutions carry over for MD, MS, MSD (where applicable)?
		4. Did all prep and analysis matrices match up?

Comments:

_____

_____

_____

Analyst Signature: _____ Date:

Reviewer Signature: _____ Date:

Attachment 5.

Known Digested QC Values (mg/L)

Element	LCS/Spike	TCLP Spike
Al	2	---
Sb	0.5	---
As	0.1	5
Ba	2	100
Be	0.05	---
Bi	0.5	---
B	1	---
Cd	0.05	1
Ca	10	---
Cr	0.2	5
Co	0.5	---
Cu	0.25	0.25
Fe	1	---
Pb	0.10	5
Mg	10	---
Mn	0.5	---
Mo	1	---
Ni	0.5	0.5
P	0.5	---
K	10	---
Se	0.10	1
Si	5	---
Ag	0.05	1
Na	10	---
Sr	1	---
Tl	0.10	---
Sn	1	---
Ti	1	---
V	0.5	---
Zn	0.5	---

Default Control Limits
LCS: 80 - 120%
Spike: 75 - 125%
TCLP Spike: >50%

Appendix A:

Requirements for DOD QSM Version 3.0
Table B-1 and Table B-6

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Inorganics (Metals)

QC Check	Definition	Purpose	Evaluation
Calibration Blank (Metals only)	Reagent water containing no analytes of interest, but acidified to the same pH as all samples	To determine the zero point of the calibration curve for all initial and continuing calibrations	Continued calibration blank responses above 2x the MDL require corrective action
CCV	This verification of the initial calibration that is required during the course of analysis at periodic intervals. Continuing calibration applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models	To verify that instrument response is reliable, and has not changed significantly from the current ICAL	If the values for the analytes are outside the acceptance criteria, the initial calibration may not be stable. Results associated with out-of-control CCV results require reanalysis or flagging
Demonstrate Acceptable Analyst Capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision	To establish the analysts' ability to produce data of acceptable accuracy and precision	The average recovery and standard deviation of the replicate must be within designated acceptance criteria.
Dilution test (Metals only)	Analysis of a positive sample, which has been diluted to a concentration 1/5th of the original, to confirm that there is no interference in the original sample analysis.	To assess matrix interference	Agreement within 10% between the concentration for the undiluted sample and 5x the concentration for the diluted sample indicates the absenxe of interferences, and such samples may be analyzed without using MSA. Results outside acceptance limits indicate a possible matrix effect. ICP: must run a post-digestion spike GFAA: must run a recovery test
Duplicate Sample	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are taken and prepared and analyzed identically.	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intralaboratory analytical process for a specific sample matrix	To provide information on the heterogeneity of the sample matrix. The greater the heterogeneity of the matrix, the greater the RPD between the sample and the duplicate
ICAL	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method	To establish a calibration curve for the quantification of the analytes of interest	Statistical procedures are used to determine the relationship between the signal response and the known concentration of analytes of interest. The ICAL must be successful before any samples or other QC check samples can be analyzed.
IDL (6010 and 6020 only)	The process to determine the minimum concentration of a substance (analyte) that an instrument can differentiate from noise. The procedure for calculating varies by method.	To provide a quarterly evaluation of instrument sensitivity	IDLs must be established before samples can be analyzed.
Interference check solutions (ICP only)	A pair of solutions containing interfering elements that are used to verify the correction factors of analytes of concern	To verify the established correction factors by analyzing the interference check solution at the beginning of the analytical sequence	No samples can be run if this check does not pass acceptance criteria
LCS containing all analytes required to be reported	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern.	To evaluate method performance by assessing the ability of the lab/analyst to successfully recover the target analytes from a control (clean) matrix.	This is a required QC Check. The inability to achieve acceptable recoveries in the LCS indicate problems with the accuracy/bias of the measurement system.
Linear dynamic range or high-level check standards (ICP only)	High-level check standard periodically analyzed to verify the linearity of the calibration curve at the upper end	To verify quantitative accuracy of data up to the high-level standard	The QC check establishes the upper linear range of the calibration
Low-Level calibration check standard (ICP only)	A reference standard that contains a quantity of analyte (greater than or equal to 3x the LOD (MDL))	To confirm the accuracy of measurements at or near the LOQ (RL), It establishes the LOQ of the calibration curve for those ICP methods that rely on single point calibration. It also may be used to validate a client's project RL	This QC check must be within acceptance criteria before any samples are analyzed.

Table B-1 cont.			
QC Check	**Definition**	**Purpose**	**Evaluation**
MS	A sample prepared by adding a know amount of targeted analyte(s) to an aliquot of a specific environmental sample	To assess the performance of the method as applied to a particular matrix	The lack of acceptable recoveries in the matrix spike often points to problems with the sample matrix. One test of this is a comparison to the LCS recoveries. If the corresponding LCS recoveries are within acceptable limits, a matrix effect is likely. The lab should not correct for recovery; only report the results of the analyses and the associated MS results and indicate that the results from these analyses have increased uncertainty
MSD	A 2nd replicate MS prepared in the lab, spiked with an identical, known amount of targeted analyte(s), and analyzed to obtain a measure of the precision of the recovery for each analyte	To assess the performance of the method as applied to a particular matrix and provide information of the homogeneity of the matrix.	When compared to the MS, the MSD will provide information on the heterogeneity of the sample matrix.
MDL Verification Check	A low-level spike taken through the prep and analytical steps at approximately 2x the MDL used to verify that the laboratory can detect analytes at the calculated MDL	To validate the MDL on an ongoing basis	If the MDL verification check fails, reprep/reanalyze at a higher level to set a higher MDL or the MDL study must be repeated.
MB	A sample of a matrix similar to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results.	To assess background interferences or contamination in the analytical system that might lead to high bias or false positive data.	This QC is used to measure lab accuracy/bias. The MB could indicate whether contamination is occurring during sample prep and analysis. If analytes are detected > ½ RL, reanalyze or B-Flag results for all samples in prep batch. For common lab contaminants, no analytes detected > RL. See DoD Box D-5; & Sec. D.1.1.1
MDL Study	The process to determine the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.	MDLs must be established prior to sample analysis. The RL or LOQ is at least 3x the MDL. Used in combination with the MDL verification check to validate the MDL on an ongoing basis.
MSA (ICP/GFAA only)	Adding known amounts of standard to one or more aliquots of the processed sample solution.	To compensate for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences that cause a baseline shift.	This is the method used when matrix interferences are present and do not allow determination of accurate sample results
Post digestion spike addition (ICP and ICP/MS only)	An analyte spike added to a portion of prepared sample to verify absence or presence of matrix effects	To confirm the presence of a matrix interference. Assess matrix effects based on: 1. the occurrence of new and unusual matrices included within the batch, or 2. contingency analysis based on SD or MS failures	To verify the absence of an interference, the spike recovery criteria is 75%-125% Results outside this criteria require MSA for all samples within the batch
Recovery Test (GFAA only)	An analyte spike added to a portion of prepared sample to verify absence or presence of matrix effects	To confirm the presence of a matrix interference. Assess matrix effects based on: 1. the occurrence of new and unusual matrices included within the batch, or 2. contingency analysis based on SD or MS failures	To verify the absence of an interference, the spike recovery criteria is 85%-115% Results outside this criteria require MSA for all samples within the batch

Table B-1 cont.			
QC Check	**Definition**	**Purpose**	**Evaluation**
Second source calibration verification	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration	The concentration of the 2nd source calibration verification, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. This independent verification of the ICAL must be acceptable before sample analysis can begin.

Notes:
1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-6: Inorganic Analysis by ICP and AA - Methods 6010 and 7000 Series

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
IDOC	Per Instrument/Analyst	DoD acceptance criteria if available; otherwise method specific criteria	Correct / Repeat for those analytes which failed criteria	NA
MDL	Annually or quarterly MDL Checks performed	40 CFR 136B; MDL verification checks must produce a signal at least 3x the instrument's noise level.	Run MDL check at higher level and set MDL higher or reconduct MDL study	NA
IDL (ICP only)	Every 3 months	Detection limits established shall be ≤ MDL	NA	NA
Linear dynamic range (LRS) or high-level check (ICP only)	Every 6 months	Within ± 10% of expected value	NA	NA
ICAL ICP: min 1 high std and a calibration blank GFAA: min 3 stds and a calibration blank CVAA: min 5 stds and a calibration blank	Daily initial calibration prior to sample analysis	ICP: No acceptance criteria unless more than 1 standard is used, in which case $r \geq 0.995$ GFAA: $r \geq 0.995$ CVAA: $r \geq 0.995$	Correct problem then repeat initial calibration	NA
2nd Source calibration verification (ICV)	Once after each initial calibration	Value of 2nd source for all analytes within ± 10% of expected value	Correct problem and verify 2nd source standard. Rerun, if that fails, correct problem and repeat initial calibration.	NA
Continuing Calibration verification (CCV)	CCV – After every 10 field samples and at end of analysis sequence. (DoD Box 58: CCV standards shall be at or below the middle of the calibration range)	ICP: within ± 10% of expected value GFAA: within ± 20% of expected value (Data associated with an unacceptable CCV may be fully usable under the following conditions: 1. CCV (high bias) and samples ND, then raw data may be reported with appropriate flag 2. 2. CCV (low bias) and samples exceed maximum regulatory limit/decision level (DoD Box 60: Project specific permission from appropriate DoD personnel is required to report data generated from a run with noncompliant CCV.)	Correct problem, rerun CCV. If that fails, repeat ICAL and reanalyze all samples since the last good CCV (DoD Box 59...if the lab chooses to demonstrate the success of routine corrective action through the use of 2 consecutive CCVs, then the concentrations of the two CCVs must be a two different levels within the original calibration curve with at least one falling below the middle of the calibration range.)	NA
Low-level calibration check standard (ICP only)	Daily, after one-point initial calibration	Within ± 20% of expected value	Correct problem, then reanalyze. No sample may be analyzed without a valid low-level calibration check standard. Low-level calibration check standard should be ≤ RL	NA
MB	One per prep batch	No analytes detected > ½ RL For common lab contaminants, no analytes > RL	Correct problem, then see criteria in box D-5; if required, reprep/reanalyze MB and all associated samples	Apply B-flag to all results for the contaminated analyte for all samples in the associated prep batch
Calibration Blank (ICB / CCB)	Before beginning a sample run, after every 10 samples, and at the end of the analysis sequence	No analytes detected > 2x MDL	Correct problem, then reprep and reanalyze calibration blank and previous 10 samples	Apply B-flag to all results for the contaminated analyte for all samples in the associated prep batch
Interference check solution (ICS) (ICP only)	At the beginning of analytical run	ICS-A: Absolute value of concentration for all non-spiked analytes < 2x MDL (unless they are verified trace impurity from one of the spiked analytes) ICS-AB: ± 20% of expected value	Terminate analysis; locate and correct problem; reanalyze ICS	NA
LCS (containing all analytes to be reported)	One LCS per prep batch	DoD specified QC criteria, if available	Correct problem, reprep/reanalyze the LCS and all samples in the associated prep batch for all failed analytes, if sufficient sample is available	Apply Q-flag to specific analyte(s) in all samples in the prep batch.

Table B-6 cont.				
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**
Dilution Test	Each prep batch or when a new or unusual matrix is encountered	5x dilution must agree within ± 10% of the original determination Note: Only applicable for samples with concentrations > 50x MDL (ICP) or > 25x MDL (GFAA and CVAA)	ICP: Perform post-digestion spike (PDS) GFAA: Perform recovery test CVAA: Perform matrix spike	NA
Post-digestion spike (PDS) (ICP only)	When dilution test fails or analyte concentration in all samples < 50 x MDL	Spike addition must produce a level between 10-100 x MDL. Recovery limit: 75-125% of expected value	Run samples by MSA or see flagging criteria	Apply J-flag to all associated sample results (for same matrix) for specific analyte(s)
Recovery Test (GFAA only)	When dilution test fails or analyte concentration in all samples < 25x MDL	Recovery limit: 85-115% of expected value	Run samples by MSA or see flagging criteria	Apply J-flag to all associated sample results (for same matrix) for which MSA was not run
MSA or Internal Standard Calibration	When matrix interference is suspected	NA	NA	NA Document in Case Narrative
MS	One per prep batch per matrix	For matrix evaluation, use DoD specified QC criteria for LCS	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample
MSD or Sample Duplicate	One per prep batch per matrix	RPD ≤ 20% (between MS and MSD or sample and sample duplicate)	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample
Results reported between LOD and LOQ			Apply J-flag to all results between LOD (MDL) and LOQ (RL)	

Notes:
1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

STL Chicago
STANDARD OPERATING PRACTICE (SOP) CHANGE FORM

Original SOP Number/Revision #: UPMV 8260B Rev 15 Last Mod ID (circle): NA (A) (B)
SOP Title: Gas Chromatography Mass Spectrometry-Volatiles SW-846 Method 8260B
Affected SOP Section Number(s): 7.3.5
Effective Date: 07/27/06

MK 080806

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Revision Number with Mod ID:

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1. Reason for SOP Change: Iowa Hygenic Lab Certification Audit Response Audit Date 04/03/06

2. Summary of Procedure Change (circle to indicate if there are attachments to this form: (No) Yes: # pages attached = _)

7.3.5 Drum/Waste Samples

These samples are normally treated as medium level soils or waste dilutions. Waste dilutions normally consist of 5 grams of sample to 5 mL of methanol. If the sample is non-miscible with methanol, mix the sample and allow sample to separate. Draw off the methanol into a screw top vial. Use a portion of this methanol extract to screen. Continue to analyze the sample as high level methanol extracts at a dilution based on screening result. If the sample is miscible with methanol, notify the PM and give detailed description of sample matrix and problems. The sample will automatically be given a 1:2 dilution factor since it was miscible with the methanol. Screen the sample and continue to analyze by the high level methanol extract procedure based on the screening results. ISS and SSS will be added prior to analysis. The lab can pre-spike the surrogates and spike compounds if client-specified to do so. As most drum/waste samples result in very high dilutions, it has been the labs experience that surrogates and Matrix spikes are most often diluted out and provide no useful information. Unless otherwise assigned to do so, surrogate and matrix spiking will take place at the time of analysis. Analysis of samples that arrive to the laboratory multiphasic in nature will not proceed until a discussion with the PM, Client and analyst has determined how the samples will be prepared and which phase or phases will be analyzed. The preparation of the sample will be documented. Any matrix problems or issues should be reported to the PM as soon as possible.

x [signature] 7-31-06
Initiated/Reviewed By: Name/Date

x Maureen D. Kuny 07/27/06
Initiated/Reviewed By: Name/Date

x [signature] 8-1-06
Approval Signature/Date: Section Manager

x Maureen D. Kuny 07/31/06
Approval Signature/Date: QA Manager or Designee

STL Chicago
STANDARD OPERATING PRACTICE (SOP) CHANGE FORM

Original SOP Number/Revision #: UMV - 8260B | Rev 15 Last Mod ID (circle): NA / (A)
SOP Title: Gas Chromatography Mass Spectrometry - Volatiles SW846 Method 8260B
Affected SOP Section Number(s): 6.4
Effective Date: 10/13/05

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1. Reason for SOP Change: South Carolina Certification - clarification on use of linear regression.

2. Summary of Procedure Change (circle to indicate if there are attachments to this form: (No) Yes: # pages attached = ___)

South Carolina does not allow use of quadratic curves for initial calibrations. The SOP will be updated to clarify that if the 15%RSD criteria is not met only the linear regression model will be used. This will be considered a project - specific requirement and state-specific requirement.

M. Kueng 10/13/05
Initiated/Reviewed By: Name/Date

Initiated/Reviewed By: Name/Date

Gary Pfeffer 10/13/5
Approval Signature/Date: Section Manager

Teresa A. Preston 10/13/05
Approval Signature/Date: QA Manager or Designee

SOP No.	Revision No.	Date	Page
UMV-8260	15	09/09/05	1 of 64

TITLE: Gas Chromatography Mass Spectrometry - Volatiles SW-846 Method 8260B

Updated by:	Signature:	Date:
Matt Kobus Technical Manager		9/8/5

Approved by:	Signature:	Date:
JoAnn Petruszak-Kmetty Supervisor, GC/MS VOA Dept.		9-8-05
David W. Mazur Env. Health & Safety Coor.		9/8/05
Terese A. Preston Quality Manager	Terese A. Preston	9/8/05

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1.0 SCOPE / APPLICATION

To outline the guidelines for the analysis of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) using SW-846 Methods 8260B and 8000B as references. The preparation of all volatile samples is based on Methods 5000 and 5030B. Method 5035 is covered by a separate SOP (USP-5035), but can also be found in this SOP.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

Specific requirements pertaining to the DOD QSM Version 3.0 are located in Appendix A. These requirements are additionally applicable to all NFESC projects. Any deviations from these procedures and/or variances from must be addressed appropriately in accordance with standard operating protocol and pre-approved on a project by project basis.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Reporting Limits

Reporting Limits [a.k.a., Estimated Quantitation Limits (EQLs)] are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported.

Table 1 defines the reporting limits and analyte list for SW-846 Method 8260B.

3. Internal interferences can be purged from the sample with the target compounds and appear as elevated baselines or distinct peaks. Internal interferences most often manifest themselves as low/high recoveries of surrogate/matrix spike compounds. Matrix interferences vary from sample to sample.
4. The volatile lab must be free of solvents. All analytes must be less than their EQL (Estimated Quantitation Limit). The volatile lab is under positive pressure to reduce lab contamination, however, intermittent low levels of acetone and methylene chloride may be detected, usually below the EQL. Refer to Section 8.2 (Corrective Action) for clarification for blank contamination.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

- The GC contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.
- There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.
- All employees will adhere to the practices and policies in the STL Corporate Safety Manual (CSM) and will read the MSDS's for the materials used in this method before handling or using the material.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: **This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Methanol (MeOH)	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.2 Summary of Method

This method is used to determine volatile organic compounds in a variety of matrices. It is applicable to water, soil, sediment, sludge and waste drum samples.

This method can be used to quantify most volatile organic compounds that have a boiling point less than 200°F. It is also limited to those compounds that elute as sharp peaks from a capillary column. A listing of applicable compounds and their characteristic ions appears in Table 2.

A portion of sample, measured into a sample vessel, is purged with an inert gas. The volatile compounds are transferred to a trap, containing retarding materials. The trap is then backflushed with the inert gas and rapidly heated to effectively transfer the compounds to the GC column. The GC oven is then, temperature ramped to separate the compounds and introduce them to the source. The mass filter separates the ions, which are then detected by the analyzer. The data system then provides qualitative and quantitative information concerning the sample.

Instrument calibration occurs about every 12-hours, or prior to analysis. Instrument maintenance is performed as needed or daily basis.

2.0 INTERFERENCES

1. External interferences can be caused by contaminants from sample containers, preparative glassware and reagents, syringes and columns and manifest themselves as high background and/or discrete peaks. Some contaminants are also introduced through the sample vial seal and/or instrument sample connections. Proper glassware preparation, sample handling and instrument maintenance should eliminate these sources. A laboratory method blank (MB) is analyzed prior to any analysis to show absence of any contaminants. Reagent (Milli-Q) water sampled in the lab and carried through all field operations is also analyzed to show absence of contaminants from field sampling.

2. Carryover is also another source of contamination. Any time a high-level sample is analyzed, the next sample in the batch is checked for carryover. If carryover is suspected, that sample is re-analyzed. The position is rinsed with methanol/water. If the carryover is excessive and continues into the next samples, the batch is aborted/paused, the column and trap baked, and/or blanks analyzed until all contamination is absent. If further response is required (i.e., trap replacement), it is documented in the maintenance database. Refer to Section 7.4 for information on preventive maintenance.

4.0 EQUIPMENT AND SUPPLIES

4.1 Current Hardware/Software

- 1 Hewlett-Packard 5890 GC interfaced with a 5972 MSD. Equipped with DB-624 column.
- 3 Hewlett-Packard 6890 GC interfaced with a 5973 MSD. Equipped with DB-624 column.
- 2 Hewlett-Packard 6890 GC interfaced with a 5975 MSD. Equipped with DB-624 column.
- 4 Tekmar 3000 concentrators, 2 OI Elcipse 4660 concentrator in connection with 8 Varian Archon Autosamplers for six systems.
- 2 Hewlett-Packard 5890 GC interfaced with a 5972 MSD. Equipped with DB-624 column used as Screeners.
- 8-Hewlett-Packard Chemstations and peripheral hardware. 2 using B.02.04 software, 2 with version D02.00 and 2 using version D00.00.
- 1-Hewlett-Packard Chemserver 9000 series running HP-UX10.2 OS with Target 3.5.

The GC/MS has a temperature programmable chromatograph interfaced with a mass-selective detector capable of scanning from 35 - 260 amu every second or less using 70 volts of electron energy in the electron ionization mode. The system is capable of producing an acceptable spectrum of bromofluorobenzene when 50 ng is analyzed.

4.2 Data System

The analytical systems are interfaced with stand alone PC's which are Pentium based systems running Agilent Chemstation. This system is capable of continuous acquisition and storage of mass spectral data. Completed data files are automatically transferred to the Chemserver Target 3.5 processing software which is capable of plotting specific masses versus time or scan numbers (Extracted Ion Current Profile) and integration of that abundance. The system also stores the data. The NBS Library resides on the Chemserver.

4.3 Data File Name/ Batch Directory Assignment

Each job # is assigned a code at the time that the first sample is analyzed. Tune, standard, blank, and laboratory control sample (LCS) data files are designated by specific letters unique to each instrument in conjunction with the appropriate month and day (example : 3a0318 = instrument #3, first 12 hour BFB tune, March 18). During transfer of the files to the Chemserver, a unique batch directory is created on Target per instrument, date and tune.

4.4 Miscellaneous

- assorted syringes (10, 25, 50, 100, 500 and 1000 uL)
- 5 mL luer-lock gas-tight syringes
- assorted purge vessels (water, 5/25 mL)

- top-loading balance, capable of weighing to ± 0.1 g, stainless steel spatula
- assorted amber and clear Teflon-lined screw-capped vials (1.5-2.0 mL, 3.5-5.0 mL)
- cleaned 40 mL vials w/Teflon-lined screw-caps
- assorted volumetrics (10 mL, 25 mL, 50 mL and 100 mL)

5.0 REAGENTS AND STANDARDS

The majority of the calibration standards are EPA certified, A2LA or second-source verified by the standard vendor in situations where suitable SRMs (Standard Reference Material) was available. For those compounds where standards must be made from neat material (due to instability) or some non-routine compounds, **where available**, a second-source is purchased and used in the LCS to verify the standard

Each time new standards are prepared and a new initial calibration is required, the standards are verified against a second-source LCS (ICV-Initial Calibration Verification standard) prior to any sample analysis. This holds for all routine compounds and those available as second-source material in the LCS.

All neat standards/kits received are entered into LabNet (LIMS) (and recorded in the Neat Standards Logbook). A code is written on the bottle/kit and entered into LabNet (and recorded in the logbook). All neat standards are then stored in a separate freezer at approximately –10°C until needed. The standard is issued a unique ID# [i.e., Neat Standards Reference Number (NSRN)] which is used to track all standards as they are used as is or in preparation of stock/working solutions. The format of the standards in LabNet will prevent working or intermediate level solutions from being used past the expiration date of the neat or stock solutions.

5.1.1 Reagent Water (Milli-Q)

1-Liter of water is continuously purged with pre-purified nitrogen. The reagent water is routinely demonstrated to be interference-free. All compounds are < EQL or 5x EQL for methylene chloride and acetone.

5.1.2 Methanol (MeOH)

All new lot numbers of P & T J.T.Baker Methanol are analyzed and verified to be free of contaminants. This information is available on the STL Oasis Web-Site that can be accessed by all analysts. The currently approved lot numbers are listed on this site. A copy of the section of the spreadsheet is posted in the GC/MS VOA Lab. Upon receipt of a case of methanol, the lot number is verified on the spreadsheet. If the lot number does not appear on the hard-copy, the analyst will go to the web-site and verify the analysis. A new spreadsheet with the most current lot number will be posted. In the case where the new lot number can not be verified electronically, the GC/MS lab will analyze a portion of the methanol, verify it to be free of contaminants, and record the analysis information in the Methanol Check Logbook.

5.2 Surrogate Spiking Solution

Working surrogates are purchased as a custom mix solutions from Restek in 5.0 mL ampules. The following surrogates are used:

Compound	Concentration
4-Bromofluorobenzene	\ 250 ppm /
1,2-Dichloroethane-d_4	
Toluene-d_8	
Dibromofluoromethane	

Upon arrival to the laboratory, the standard is entered into LabNet. When the ampule is opened, the transfer to the surrogate vial on the Archon Autosampler is entered into LabNet (and recorded in the Standard Preparation Log). The standard issued is another unique ID# [i.e., SRN (Standard Reference Number)] which can be traced back to the parent ID# (i.e., NSRN with the date of receipt, date of opening, and the supplier).

- Life of Standard: 1-year unopened; once opened, they are used for a period of 14 days or until used.
- Storage Requirements: Stored in a freezer at ~ –10°C in the dark and kept for a period of one year unopened. *

5.3 Internal Standard Spiking Solutions

Working internal standards are purchased as a custom mix solutions from Restek in 5.0 mL ampules. The following internal standards are used:

Compound	Concentration
Pentafluorobenzene	\ 250 ppm /
Chlorobenzene-d_5	
1,4-Difluorobenzene	
1,4-Dichlorobenzene-d_4	

After opening, the mixture is transferred to the internal standard vial on the Archon autosampler. The transfer is entered into LabNet (and recorded in the Standard Preparation Log). The standard issued is another unique ID# [i.e., SRN (Standard Reference Number)] which can be traced back to the parent ID# (i.e., NSRN with the date of receipt, date of opening, and the supplier).

- Life of Standard: 1-year unopened or manufacturers expiration; once opened, they are used for a period of 14 days or until used.
- Storage Requirements: Stored in a freezer at ~ –10°C in the dark and kept for a period of 1-year unopened. *

Purgeables
Calibration Standards

VOC Custom Mix (No Gases)
100 ug/mL in MeOH

1,1,1,2-Tetrachloroethane
1,1,1-Trichloroethane
1,1,2-Trichlorotrifluoroethane
1,1,2,2-Tetrachloroethane
1,1,2-Trichloroethane
1,1-Dichloroethane
1,1-Dichloroethylene
1,1-Dichloropropylene
1,2,3-Trichlorobenzene
1,2,3-Trichloropropane
1,2,4-Trichlorobenzene
1,2,4-Trimethylbenzene
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
1,2-Dichlorobenzene
1,2-Dichloroethane
1,2-Dichloropropane
1,3,5-Trimethylbenzene
1,3-Dichlorobenzene
1,3-Dichloropropane
1,4-Dichlorobenzene
2,2-Dichloropropane
2-Chlorotoluene
4-Chlorotoluene
4-Isopropyltoluene
Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Carbon tetrachloride
Chlorobenzene
Chloroform
Chlorohexane
cis-1,2-Dichloroethylene
cis-1,3-Dichloropropylene
Dibromomethane
Dibromochloromethane
Dichloromethane
Ethylbenzene
Hexachlorobutadiene
Isopropylbenzene
m-Xylene
n-Butylbenzene
n-Propylbenzene
Methyl-tert-butyl ether
Naphthalene
o-Xylene, p-Xylene
sec-Butylbenzene
Styrene
tert-Butylbenzene
Tetrachloroethylene
Tetrahydrafuran
Toluene
trans-1,2-Dichloroethylene
trans-1,3-Dichloropropylene
Trichloroethylene

ICAL 2 STD Custom Mix
100 ug/ml in MeOH
2-Methylnaphthalene
1,3,5-Trichlorobenzene
1,3-Butadiene
Isopropylether
Methyl Acetate
Hexane
Heptane
Cyclohexane
Ethyl ether
Methyl Cyclohexane

APIX Custom STD
2000, 8000 & 10000 ug/mL
Allyl Chloride
Ethyl Methacrylate
Methyl Methacrylate
Methacrylonitrile
Pentachloroethane
Trans-1,4-Dichloro-2-Butene
Iodomethane
Isobutanol
Cyclohexanone
n-Butanol
2-Nitropropane
Ethyl Acetate

Chloroprene
5000 ug/mL

SS Volatile Organic Compound Mix
2000 ug/mL in MeOH
Chloroethane
Methyl Bromide (Bromomethane)
Methyl chloride (Chloromethane)
Trichlorofluoromethane
Dichlorodifluoromethane
Vinyl chloride

Vinyl Acetate
2000 ug/mL in MeOH

Volatile Custom Ketone Mix
Acetone
2-Hexanone
Methyl ethyl ketone
4- Methyl-2-pentanone
Carbon Disulfide
100 ug/mL in MeOH

Nitriles and Acrolein Custom Mix
Acetonitrile 800 ug/mL in Water
Acrylonitrile 800 ug/mL in Water
Propionitrile 800 ug/mL in Water
Acrolein 4000 ug/mL in Water

2-Chloroethylvinylether
2000 ug/mL in MeOH

5.4 Stock Purgeable Standards

These are obtained as custom mixes from Restek and Supelco. The contents of each solution and concentration appear on the previous page. Upon opening, all contents are transferred to 1.5-2.0 mL amber, Teflon-lined screw-capped vials. Listed are compounds in the EPA TCL and includes compounds done on a regular basis. Other standards, if needed, are either purchased as neat solutions or neat standards from Supelco, Chem Service or other certified supplier. See appropriate entries in LabNet.

* If the stock solution has manufacturers' expiration date, that is assigned. If the date is not evident, 1-year is assigned to un-opened ampules. This is applicable for all "neat" standards.

5.4.1.1 Main 8260 Mix

The 8260 Working Standard is a vial transfer:

Compound / TCL Mix	Volume[1] (mL)	Concentration
8260 Custom Mix Stock/Working Std	1	100 ppm each component

5.4.1.2 Gases

The Gas Working Standard is prepared as follows:

Mix	Volume (uL)	MeOH	Concentration
2000 ppm Gas Mix	100	Dilute to 2 mLs	100 ppm each component

5.4.1.3 Additional Compounds

The Ketone and Acrolein/Nitrile Working Standards are vial transfers:

Compound / TCL Mix	Volume[1] (mL)	Concentration
Ketone Custom Mix Stock/Working Std	1	100 ppm each component

Compound / TCL Mix	Volume[1] (mL)	Concentration
Nitriles/Acrolein Custom Mix Stock/Working Std	1	800 ppm Nitriles 4000 ppm Acrolein

The CEVE and Vinyl Acetate Working Standard are prepared as follows:

Stock Compound/Mix	Volume (uL)	MeOH	Concentration
2000 ppm CEVE	100	Dilute to 2 mLs	100 ppm each component
2000 ppm Vinyl Acetate	100		

5.4.1.7 Appendix IX

The Appendix IX and extra compounds are prepared as follows:

Compound / TCL Mix	Volume[1] (mL)	MeOH	Concentration
APIX Custom Stock Standard	250ul	Diluted to 2mLs	250/1250/10000 ppm

The ICAL 2 Custom Working Standard is a vial transfer:

Compound / TCL Mix	Volume[1] (mL)	Concentration
ICAL2 Custom Mix Stock/Working Std	1	100 ppm each component

- Life of Standard: Unopened ampules are assigned the manufacturer's expiration date or 1 year from receipt. Working solutions have an expiration date of 1-week (Gases) and 2-weeks for all others.
- Storage Requirements: These mixtures are stored in 1.5-2.0 mL amber Teflon-lined screw-capped vials at ~ –10 °C in the dark

NOTE: All standard 'recipes' are listed here in this SOP for guidelines for standard preparation. These 'recipes' are subject to change.

5.4.1.8 Low Level Standard

A low level standard is prepared by making a 1/10 dilution of the stock standards of each of the above (nitriles and acrolein included). This standard is used to prepare the low points in the initial calibration. The low level standard may contain the Main 8260 Mix, gases, nitriles and acrolein, and any other required standard. A low-level standard for the Appendix IX compounds is also prepared separately due to duplication of some compounds.

A low level surrogate solutions is also prepared by a 1/10 dilution of the working for low points in the water curve. The calibration levels may vary with the compounds. See recipes in the calibration section for the levels. The low point in the calibrations is based on each compounds reporting limit.

All solutions are stored in a 1.5-2.0 mLs amber Teflon-lined screw-capped vials at –10°C in the dark. All standard preparation is recorded in the LabNet system. Solutions are prepared every 2-weeks (1-week for the gases; 1-month for the nitriles).

Purgeable Spike Standard Mixes
ACCUSTANDARD and Absolute Standard

VOC LIQUID MIXTURE
2000 ug/mL in MeOH

1,1,1,2-Tetrachloroethane
1,1,1-Trichloroethane
1,1,2,2-Tetrachloroethane
1,1,2-Trichloroethane
1,1-Dichloroethane
1,1-Dichloroethylene
1,1-Dichloropropylene
1,2,3-Trichlorobenzene
1,2,3-Trichloropropane
1,2,4-Trichlorobenzene
1,2,4-Trimethylbenzene
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
1,2-Dichlorobenzene
1,2-Dichloroethane
1,2-Dichloropropane
1,3,5-Trimethylbenzene
1,3-Dichlorobenzene
1,3-Dichloropropane
1,4-Dichlorobenzene
2,2-Dichloropropane
2-Chlorotoluene
4-Chlorotoluene
4-Isopropyltoluene
Benzene
Bromobenzene
Bromoform
Carbon tetrachloride
Chlorobenzene
Chlorodibromomethane
Chloroform
cis-1,2-Dichloroethylene
cis-1,3-Dichloropropylene
Dibromomethane
Dichlorobromomethane
Dichloromethane
Ethylbenzene
Hexachlorobutadiene
Isopropylbenzene
m-Xylene
n-Butylbenzene
n-Propylbenzene
Naphthalene
o-Xylene
p-Xylene
sec-Butylbenzene
Styrene
tert-Butylbenzene
Tetrachloroethylene
Toluene
trans-1,2-Dichloroethylene
trans-1,3-Dichloropropylene
Trichloroethylene

Bromochloromethane
2000 ug/mL in MeOH

Heptane
2000 ug/mL in MeOH

MTBE
2000 ug/mL in MeOH

1,3,5-Trichlorobenzene
2000 ug/mL in MeOH

Clorohexane
1000 ug/mL in MeOH

Ethyl Ether
1000 ug/mL in MeOH

Hexane
1000 ug/mL in MeOH

Trichlorotrifluoroethane
2000 ug/mL in MeOH

Volatile Organic Compound Gas Spike
2000 ug/mL in MeOH
Chloroethane
Methyl Bromide (Bromomethane)
Methyl chloride (Chloromethane)
Trichlorofluoromethane
Dichlorodifluoromethane
Vinyl chloride

Volatile Mix Additional Spike Compounds
2000 ug/mL in MeOH
Acetone
2-Hexanone
Methyl ethyl ketone
4- Methyl-2-pentanone
Carbon Disulfide
Vinyl Acetate
2-Chloroethylvinylether
Iodomethane

THF
2000 ug/mL in MeOH

5.5 Stock Matrix Spike Solution

The matrix spike compounds are obtained as solutions from a second source (i.e., Accustandard) in 1.5-2.0 mL ampules. These are listed on the previous page. A different analyst than the one who prepared the calibration solutions usually prepares matrix spike solutions. These are stored at ~ -10°C in the dark prior to use. Neat standards are kept for a period of 1-year un-opened or the manufacturer's expiration date. Once opened, the stock may be used for 3-months.

The matrix spike solutions are prepared as follows:

5.5.1 VOC Spike

Stock Compound/Mix	Volume (uL)	MeOH	Concentration
2000 ppm VOC Liquid Spike	25	Dilute to 1 mL	50 ppm each component
2000 ppm 8260 Additional Spike	25		
1000 ppm 1,3,5-Trichlorobenzene Spike	50		

5.5.2 Gas Spike

Mix	Volume (uL)	MeOH	Concentration
2000 ppm Gas Spike	50	Dilute to 2 mLs	50 ppm each component

5.5.3 Additional Spike Compound Mix

Compound	Volume[1] (uL)	MeOH	Concentration
2000 ppm Bromochloromethane	25	Dilute to 1 mL	50 ppm each component
1000 ppm Ethyl Ether	50		
1000 ppm Chlorohexane	50		
1000 ppm Hexane	50		
2000 ppm MTBE	25		
1000 ppm Heptane	50		
1000 ppm Trichlorotrifluoroethane	50		

5.5.4 Tetrahydrafuran Spike

Mix	Volume (uL)	MeOH	Concentration
2000 ppm Tetrahydrafuran	50	Dilute to 1 mL	100 ppm

For waters, addition of 5 uL of each solution results in all spike compounds at 10 ppb, with the exception of THF which is at 20 ppb for a 25mL purge volume.

For soils, addition of 5 uL of each solution, except THF at addition of 2.5 uL, results in all compounds at 50 ppb.

These solutions are stored at ~ -10°C in several 1.5-2.0 mL amber Teflon-lined screw-capped vials. All standard preparation is recorded in the LabNet system. Working matrix spike solutions have a 2-week/1-week (Gases) expiration date or until low recoveries of the matrix spike compounds indicate a new solution is needed. See above for label information.

5.6 Stock BFB Solution

The BFB standard is purchased as a neat solution from Supelco.

Stock	Amount	MeOH	Concentration
2000 ppm BFB	25 uL	Dilute to 2 mLs	25 ppm

- Life of Standard: This stock can be kept for a period of 1-year until opening. Upon opening, the solution is transferred to a 1.5 - 2.0 mL vial and assigned an SRN. Once opened, it is used for a period of 6-months.
- Storage Requirements: The standard is stored at ~ –10°C in the dark

Addition of 2 uL to 5 mLs results in a concentration of 50 ng/5 mLs.
All preparation is recorded in the LabNet system. All labels are completed as above.

NOTE: Intermediate and Working Solutions are never assigned an expiration date exceeding the expiration date of the neat/stock standards/solutions.

6.0 CALIBRATION

Before an instrument is used as a measuring device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument. Preparation of all reference materials used for calibration is documented.

6.1 PFTBA Autotune or Manual Tune

The instrument is first tuned in one of two ways: autotune or manual tune. The ion abundances in the calibration gas are best monitored near the temperature of analysis of BFB. Monitoring at this temperature produces the most representative cal gas scan and therefore the best estimate of BFB response.

1. If an AUTOTUNE is to be performed, continue below. If not, skip to step 6. An autotune is not run before every initial calibration. If the instrument has been down for any reason previously listed or major difficulties in manual tune are encountered, an autotune is performed. Autotunes are generally NOT performed when an existing initial calibration is being met.

2. The Chemstation software has a menu driven tune program. Begin the autotune program. Key masses are 69, 219 and 502.

3. Follow instructions and retrieve a hardcopy of the autotune results. Check the following:

- passed/fail: in itself, not necessarily an indication of MS performance
- repeller and ion focus settings
- electron multiplier voltage

4. The repeller and EM voltages are good indicators of the sources' cleanliness. Generally, the lower the setting the cleaner the source. Other factors may however, supersede (i.e., the age of the multiplier) and a clean source will not always autotune these low. The EM is set by autotune program to produce a target abundance for mass 69 (varies depending on the tune program and instrument). The operator may plan on having to increase this by 100-200 to achieve normal analysis sensitivity (depends on the tune program and the instrument).

5. Observe peak shape, absence of lead-ons/tailing, the resolution between isotopes, peak width and mass axis. A hardcopy of the profile scan is desirable, and can be filed with the autotune results.

6. If an AUTOTUNE has just been performed, continue here. If not, skip to step 9. Enter MANUAL TUNE and read the autotune (which was automatically stored in a file). For volatiles, edit the scan parameters to monitor ions 69, 131 and 219.

7. Enter one of several methods available and adjust the parameters (usually the ion focus, entrance lens and amu gain) to achieve the following relative abundances:

Mass	Relative Abundance
69	100%
131	32-40%
219	35-45%

These will vary with the MS. Mass 219 is usually 5-9% greater than mass 131. If necessary, adjust the amu gain for peak shape and high-end isotope resolution. An overall peak-width of 0.500 is desirable.

Again, these adjustments and relative abundances may not guarantee that BFB will meet requirements, but is a good place to start.

8. A hardcopy the profile scan is desirable. This can be filed with the autotune results. This file can serve as a diagnostic tool and can also provide a starting point in the event the operator has trouble meeting the initial calibration.

Save the changes to the appropriate Tune File. Exit the program.

9. If an AUTOTUNE has not been performed, enter MANUAL TUNE and adjust any parameters, if need be. Adjustment may not be necessary, and not desirable, if problems in tuning or meeting the initial calibration have not been encountered. A hardcopy of profile scan can be printed and filed. Save the changes and exit the program.

6.2 BFB Analysis

Once the instrument is tuned, 50 ng of 4-Bromofluorobenzene must meet criteria. The BFB can be purged or directly injected. The mass spectrum must meet the following criteria:

Mass	Ion Abundance
50	15-40% of mass 95
75	30-60% of mass 95
95	Base Peak, 100% rel. abund.
96	5 - 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 - 9% of mass 174
176	>95% but <101% of mass 174
177	5 - 9% of mass 176

The BFB is analyzed by one of the methods in Attachment 1. **(Method parameters listed in the appendices are examples only. This statement applies to all references made to these methods).** Typical Concentrator conditions also appear in Attachment 1. The EM voltage may be 100-200 volts above autotune. The abundances of the designated masses above MUST meet the criteria before analyses can begin. If necessary, enter MANUAL TUNE and adjust parameters. BFB analysis is completed about every 12-hours of analysis.

6.3 Description of Initial Calibration

An initial calibration may be completed:

- as needed - continuing calibration can not be met
- after a source cleaning and/or column change or any time a major repair or change has occurred with the instrument that affects calibration where a new calibration is indicated.

Confirm that the GC/MSD is stable and equilibrated. If at all possible, allow the instrument to equilibrate overnight at all operating temperatures if the source/column has been cleaned/changed. Prior to beginning initial calibration it is a good idea to:

- check the background of air/water levels and base ion by scanning for appropriate ions and also visually inspecting the spectrum scan for any other possible and undesirable background.
- recheck the multiplier settings, after a source is cleaned the EM can most often be dropped.

6.4 Initial Calibration

Each calibration standard is analyzed according to one of the methods in Attachment 1. These are examples. The actual number of points in the calibration is determined by the calibration and acceptance criteria table (Attachment 4). The EM voltage may be 100-200 volts above autotune.

Allow standards to come to ambient temperature.

Fill ten 5-mL or 10-mL luer-lock gas-tight syringes with reagent water to overflowing. Replace the plunger and invert. Adjust to 5-mL or 10-mL, confirming the absence of any air bubbles. Pull back slightly on the plunger to allow addition of standards. Use the following as guides :

Soils: 5-mL Purge Volume Water: 10-mL Purge Volume

Concentration					Preparation in uL				
Main Mix/Gas / MTBE/Other	Extra	Nit	Acrol	APIX	Main Mix/Gas/ MTBE/THF/ Extra/Other (100 ppm)	Surr. 50 ppm	Nit/Acrol 800 / 4,000 ppm	APIX 250 ppm	ICAL 2 100 ppm
2/1	2/1	NA [1]	NA	NA	2 (LL)	2 (LL)	1 (LL)	1 (LL)	2 (LL)
5/2.5	5/2.5	40/20	200/100	10/5	5 (LL)	5 (LL)	2.5 (LL)	2 (LL)	5 (LL)
20/10	20/10	160/80	800/400	40/20	20 (LL)	20 (LL)	10 (LL)	8 (LL)	20 (LL)
30/15	30/15	240/120	1200/600	50/25	30 (LL)	30 (LL)	15 (LL)	10 (LL)	30 (LL)
50/25	50/25	400/200	2000/1000	100/50	2.5	5	2.5	2	2.5
70/35	70/35	560/280	2800/1400	150/75	3.5	7	3.5	3	3.5
100/50	100/50	800/400	4000/2000	200/100	5	10	5	4	5
150/75	150/75	1200/600	6000/3000	300/150	7.5	15	7.5	6	7.5
200/100	200/100	1600/800	8000/4000	400/200	10	20	10	8	10

[1] Stocks referred to here are listed on pages 7 thru 12, and include the regular compounds, Gas, Extra compounds, Appendix IX, Nitriles and Acrolein. The Appendix IX curve must be analyzed separately.

Immediately add the standards to a clean 40-mL vial. Following the parameters in Table 1, analyze the 50 ppb standard (soil samples) or the 25 ppb standard (water samples). A normal standard will appear very similar to the ones in Figures 1 and 2. Quantitate the standard against the appropriate method file. A short list example of one file appears in

Attachment 2. Sufficient areas for the first internal standard will vary somewhat between instruments. Acceptable areas should be based on maintaining sufficient sensitivity for poor responders without saturating the detector at the upper end of the calibration range. Too low an area will almost guarantee poor/unsatisfactory responses of low-response compounds and too high an area will result in saturation of some compounds at higher levels, resulting in false low response factors at high concentrations.

It is helpful to analyze a medium level standard first and assess the areas before continuing with the low/high level standards.

Response factors are calculated by the data system as follows:

$$RF = \frac{A_x \times Q_s}{A_s \times Q_x}$$

Where:
A_x = ion abundance for analyte
A_s = ion abundance for its internal standard
Q_s = concentration of its internal standard
Q_x = concentration of analyte
(Response Factors have no units)
The appropriate quant ion must be in the method file. See an example of a file in Attachment 2. A listing of the target compounds with their appropriate internal standards also appears in Attachment 2. Confirm the presence of all targets and the separation of non-co-eluting compounds. Note the response factors for the gasses. If necessary, prepare new standards.

If adjustments to the acquisition parameters are necessary, make them and re-analyze the 50 ppb standard (soil samples) or the 25 ppb standard (water samples).

When a standard is analyzed and processed on target as part of the initial calibration the RF's are automatically updated in the daily method. After all initial calibration standards are processed, checked and confirmed as being accurate and passing method criteria, the initial calibration is saved to the source method. This ensures that the correct initial calibration is used for each ensuing continuing calibration check. A hardcopy of the calibration report is generated. All method criteria are assessed for compliance. Confirm that 1) all CCC's are below 30% and 2) the RF's for all SPCC compounds are >0.300 (Minimum RF for Chloromethane, Bromoform and 1,1-Dichloroethane is 0.100).
Calibration curves are evaluated following the "Evaluation and Acceptance Criteria" table (Attachment 4). For all compounds in the initial calibration with a %RSD > 15.0%, calibration curves of area ratio versus concentration using a first or higher order regression curve of the calibration curve points will be performed.

Method 8000B/8260B specifies a minimum coefficient of determination (R) of 0.990. The methods also specify a minimum of 5 calibration points for a linear model and a minimum of 6 calibration points for a higher order regression. The laboratory, in order to

meet AFCEE requirements, will analyze a minimum number of points to satisfy both the new SW846 and AFCEE. All efforts will be made to meet the minimum COD of 0.990. However, there are some compounds that historically present a problem meeting this requirement. These compounds are usually those listed in the analyte table of Method 8260B with qualifying remarks. Many of these have various known (or unknown) issues that would effect reproducibility (i.e., Acetone qualifier pp = poor purger). These typically include many of the Appendix IX compounds as well. The laboratory will take minimal action for these compounds.

The preparation instructions noted above will be modified to include the necessary calibration levels. These instructions are for guidance only and may change as needed.

An example of an acceptable initial calibration appears in Attachment 2. The BFB tune, and all standard raw data are kept near the instrument if current, otherwise can be found in a file. Each instrument has its own initial calibration.

NOTE: The actual number of points in the calibration and the low point in the calibration may vary with client and project need. Clients may have additional requirements, which would be covered in a client-specific or regulatory/agency QAPP.

6.5 Daily or Continuing Calibration

Continuing calibration occurs prior to analysis.

If time remains after the initial calibration, and the 50 ppb standard (soil samples), 25 ppb standard (10 mL water samples) meets continuing calibration criteria, samples can be analyzed up to the 12-hour tune limit. The samples are quantitated against the average RF or appropriate as per method. See later sections describing calculations.

After having satisfied BFB tune requirements, a continuing calibration standard must be analyzed. Analyze a 50 ppb (soil samples) or 10 ppb (water samples) standard following the procedure outlined above. Confirm Form 7 that all CCC's are <20% Drift and the RF's for all SPCC's are >0.300 (Minimum RF for Chloromethane, Bromoform and 1,1-Dichloroethane is 0.100). If so, the continuing calibration is acceptable and analysis can begin.

If continuing calibration can not be met, either new standards and/or a new calibration are needed.

NOTE: Method 8260B stipulate that if the CCC's are not part of the analyte list then all compounds being reported must be < 20% drift.

All internal standard areas and retention times are assessed immediately after calibration. Areas and times compared to the mid point of the initial calibration. Internal standard

areas should not deviate by a factor of two or the retention times should not deviate by > 30 s. If the situation occurs, appropriate action is taken and the standard re-analyzed. All corrective action and return to control are documented in the CAR logbook for the appropriate instrument.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Control is accomplished through 1) daily tuning and calibration checks and 2) preparation QC traceable through individual batches.

7.1.1 Initial Calibration

PFTBA BFB TUNE	Prior to Initial Cal	*limits in Section 6.2
200 or 40 ng \ 150 or 20 ng | 100 or 14 ng | 70 or 10 ng | 50 or 8 ng | 30 or 5ng | 20 or 2 ng | 5 or 1 ng | 0.5 ng /	Initial Cal need dependent on situation.	*limits in Section 6.4

NOTE: As stated, the actual number of points in the calibration and the low point in the calibration may vary with client and project need. Minimum number of points for AFCEE and/or 3rd Edition SW-846 may be 6 or 7 depending on matrix. Other clients may have additional requirements, which would be covered in a client-specific QAPP.

7.1.2 Method Blank (MB)

Prior to any analysis, the reagent water must be shown to be free of interference's and target compounds.

A 5 mL or 10 mL portion of reagent water is analyzed using one of the methods in Attachment 1. Internal Standards (ISS) and Surrogates (SSS) will be added prior to analysis. Initial concentrations of both surrogate and internal standard solutions shall be such that "sample concentrations" of the analytes conform to the method and surrogate tables provided in this SOP. All target compounds must be less than the quantitation limit (See Section 2.0). Once the MB analysis is complete and acceptable, analysis can proceed.

7.1.3 Daily Analysis

PFTBA		
BFB	Prior to continuing	* See above calibration
Daily Calibration Standard	Prior to samples	* See Section 6.5
Samples *		

*Any given 12-hour period contains a tune, standard, blank and LCS. Preparation QC is at a 5% frequency. Instrumental controls are outlined above and further discussed in the procedure section.

Prep QC	Frequency
MB	Prior to analysis
LCS	1 set per analysis batch (see below *)
MS/MSD's[1]	at least 1 set in 20
Surrogates	every blank, sample and QC Sample
QC Charting	LCS/LCD[2] set per frequency to satisfy charting requirements.

[1] The sample selection for MS/MSD, if not specified by the client on the chain-of-custody, is rotated among client samples so that various matrix problems may be noted and/or addressed.
[2] LCS Duplicate (LCD) is performed when insufficient sample is available for an MS/MS.

7.2 Sample Preservation and Storage

Sample containers, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance and/or specific contract or client requests. Listed below are the holding times and the references that include container and preservation requirements for compliance with the Resource Conservation and Recovery Act (RCRA).

Matrix	SW-846
All	14-days

All samples received for volatile analysis are refrigerated upon receipt at 4±2°C. Refrigeration is the only preservative for 5030 soil samples, while water samples are additionally preserved with 3 drops of 36% HCl to a pH >2. Water samples marked as un-preserved are analyzed within 7-days.

7.3 Sample Preparation / Screening /Analysis

Once the samples are logged into the (LIMS) database upon receipt, a paperwork trail is initiated. The Section Manager, Unit Leader or Analyst prints and prepares the necessary information (Sample Tracking Sheets/Big Boards) and places it in the appropriate file bin

in the GC/MS VOA lab. The analysts take this information and subsequently screen the associated samples. Samples are screened by MSD prior to analysis. In some cases, the GC/FID analysis can be used as a screen. The actual screening procedures vary due to sample appearance, sample matrix, client history and analytical method. Once the samples are screened, the paperwork is transferred to a second file appropriately labeled. This file contains information about samples that have been screened but need to be reviewed. Once screened, an 'X' is placed on top of the vial, indicating both that the sample has been screened, and that the particular vial can not be used for subsequent analysis. The screened analysis can be reviewed on screen or hard-copy, as all screening data is collected and stored on the data system as with all GC/MS analyses. Upon review, the analyst makes decisions concerning the screen and indicates if an initial dilution is required. This information is physically recorded on the paperwork. Once reviewed, the paperwork is then placed in appropriate files that are broken down by matrix and method. The samples are now ready to be analyzed.

7.3.1 Waters

1. Allow samples and standards to come to ambient temperature. Observe all vials of sample and confirm the absence of any air bubbles. If a vial has an air bubble do not use that vial and notify the Supervisor of the situation. Make sure the vial used for screening is properly marked and do not use this vial for analysis.

2. Remove the plunger from a 25 mL luer-lock gas-tight syringe and fill to near over-flowing. Replace the plunger. The pH of all samples is verified at time of analysis. If the pH < 2, a check-mark is placed in the appropriate column in the logbook. If the pH > 2, the actual estimated pH is written in the same column. pH checks and verification of hold-times are documented on the review form. Samples lacking preservation may be noted in the case narrative. Invert the syringe, and adjust the volume to 5 or 10 mLs. Confirm the absence of all air bubbles.

3. Immediately add the sample to a clean 40-mL vial. ISS and SSS will be added by prior to analysis. Initial concentrations of both surrogate and internal standard solutions shall be such that "sample concentrations" of the analytes conform to the method and surrogate tables provided in this SOP. Using the method described in attachment 1 analyze the sample.

4. If a batch is going to be analyzed, which is usually the case, load all samples following the procedure above. After the batch is loaded, replace all samples and standards back in storage.

5. If a dilution is required as indicated from the screening results, the following guidelines are followed. If the dilution is > 1/100 (250 uL of sample) an initial dilution is made into a volumetric flask. If serial dilutions are required, no less than 1 mL is taken for further dilutions. The final sample aliquot taken for analysis from the volumetric is no less

than 250 uL. If the dilution is < 1/100, the appropriate sample amount is added directly to the 25 mL syringe.

6. Opened sample vials are used only once unless: (a) any necessary dilutions/reruns are done the same day or (b) there are no other vials for that sample.

7.3.2 Soils

1. As some clients still request method 5030 at the present time, soils are still being analyzed as indicated below. As clients convert to Method 5035 completely, this section will be removed.

2. Before weighing any samples, check the balance using the appropriate class weights. Record the actual weights in the Balance Logbook. If a problem is noted, contact the QC department.

3. Allow samples and standards to come to ambient temperature.

4. Weight out 5 grams of the sample into a clean 40-mL vial. Add 5-mL reagent water into vial. IS/SS will be added though the septum. The autosampler will add an additional 10-mLs of reagent water. Initial concentrations of both surrogate and internal standard solutions shall be such that "sample concentrations" of the analytes conform to the method and surrogate tables provided in this SOP. Using the methods described in Attachment 1, analyze the sample. All soil samples are analyzed with a heated purge (40°C).

5. If a batch of samples is to be analyzed, prepare each as above. After the batch is loaded, replace all samples and standards in storage.

6. Any sample that based on screening results/historical data has shown to contain high concentrations of compounds is analyzed at an initial dilution. Any sample that after the initial run contains targets above the calibration range is diluted to accurately quantitate those compounds. If an initial analysis over-diluted the given sample it is re-analyzed as a low level soil. If the low-level analysis contains compounds above the calibration range, and the same compounds are within range in the dilution, both sets of data may be reported to the client.

7. If a 1/2 or 1/5 dilution is required, 2.5g/1.0g of sample is weighed into the purge vessel.

7.3.3 Medium-Level Soil Extracts

1. If a larger dilution is required, a medium-level soil extract is prepared as follows. Five grams of sample is weighed into a tarred vial. Five 5-mLs of MeOH is added to the vial and the vial sealed. After the 24-48 hour contact time, the MeOH portion is decanted

and stored in a 1-1.5 mL Teflon-lined screw-capped vial for storage. A portion of the extract (100 uL maximum) is taken for analysis. ISS and SSS will be added though the septum prior to analysis. Initial concentrations of both surrogate and internal standard solutions shall be such that "sample concentrations" of the analytes conform to the method and surrogate tables provided in this SOP. Serial dilutions, if needed, are made from the extract and appropriate amounts taken for analysis.

2. If the sample upon which a medium-level prep as been performed also required an MS/MSD, the appropriate amount of MS solution is also added.

3. All samples prepared in this manner will be analyzed against a medium-level soil curve. The standards, blanks and LCS samples will contain 100 uL MeOH. The curve will be at ambient temperature.

NOTE: Some soils are analyzed initially at low levels due to increasing client requests for lower reporting limits. The same samples may then require large dilutions to bring compounds into the calibration range of the instrument. Some compounds, most notably the ketones, have very different responses when heated versus non-heated, despite the sample matrix. Traditionally, the lab heats soils. Therefore, the match between original analyses and dilutions for compounds such as these may not appear to correlate.

Dilution	Sample Weight	Vol. MeOH (1/2.5) Extract
1/2	2.5 grams	---
1/5	1.0 gram	---
1/50	5 grams / 5 mLs	100 uL
1/250	5 grams / 5 mLs	20 uL
1/500	5 grams / 5 mLs	10 uL

4. Using those parameters in Attachment 1, analyze all samples in the batch.

5. Sample vials/jars are only used once unless: (a) any dilutions/reruns are analyzed the same day or (b) there is only one jar for analysis.

7.3.4 Method 5035

NOTE: ICAL Standards are prepared with 5 mL milli-Q water.

1. Samples for low level VOA soil analysis may be received at the lab in one of three manners: First, as replicate 5 gram core samples in 40 mL vials containing a Sodium Bisulfate preservative solution (refer to USP-5035 for collection/preservation). Secondly, as replicate 5 gram core samples in 40 mL vials containing organic free water. Thirdly, unpreserved 5 gram core samples may be received in Encore containers. These core samples must be placed in the bisulfate preservative solution or organic free water (if the effervescence test is positive) within 48-hours of collection. This time requirement is

currently under review by appropriate regulatory agencies and may be extended beyond the 48-hours. Until such time, the laboratory will endeavor to "fix" the sample cores in preservative within 48-hours of collection. The laboratory may receive replicate 5 gram soil cores to be used for reanalysis if needed.

2. In addition to low level samples, an additional soil aliquot should be received for use as a screen and possible use as a mid-level extraction/analysis. This additional core must also be fixed in MeOH within 48-hours of collection. The amount of MeOH added must closely correspond to a soil to solvent ratio of 1:1. Though not specified in the method, STL will pursue a goal of removing the MeOH from the soil within 24-48 hours after the initial extraction. A portion of the MeOH be removed and placed in an amber 1.5 - 2.0 mL Teflon-lined screw-capped vial for storage. This time limit should standardize the amount of time the MeOH comes in contact with the sample.

3. MeOH extracts of soils will be analyzed as stated above at ambient-temperature against a medium-level soil initial calibration. All surrogate and internal standard solutions will be added at time of analysis by the Archon.

4. Low level soils will be analyzed using the Closed Purge and Trap Auto Sampler System. Surrogate and internal standard solutions will be added at the time of analysis. Initial concentrations of both surrogate and internal standard solutions shall be such that "sample concentrations" of the analytes conform to the method and the spike and surrogate tables provided in this SOP. The concentration of the solution and amounts spiked may vary depending on the precision obtained with a given solution/volume combination. However, the final concentrations of such compounds in the samples will follow the same guidelines as previously stated in this SOP for all other samples.

5. As with the internal standard and surrogate, all QC spike solutions must also be added to the closed sample container. This is accomplished by the addition of the spike solutions through the septum with a small gauge (10 uL) syringe just prior to the sample being placed on the instrument for analysis.

6. Some calcareous matrices may react with sodium bisulfate and cause effervescence. The method indicates that such samples need to be recollected without sodium bisulfate preservative and analyzed within 48-hours of collection. Alternatively, some clients and/or regulatory agencies allow optional preservation and holding time criteria. On a per project basis, samples that react with sodium bisulfate may be collected and placed in vials containing water without the preservative. The vials are kept ≤ -12 °C until analysis. Such samples must be thawed prior to analysis. The maximum holding time for this type of collection and preservation is 14-days from the collection date. This alternative approach must be approved by the client/project prior to use.

7.3.5 Drum/Waste Samples

- Non-MeOH Miscible
- MeOH Miscible

These samples are normally treated as medium level soils or waste dilutions. Waste dilutions normally consist of 1 gram of sample diluted to 10 mLs of MeOH. Serial dilutions, if needed, are made from this extract. A portion of the extract is then added to the 5 mL syringe. ISS and SSS will be added prior to analysis. Initial concentrations of both surrogate and internal standard solutions shall be such that "sample concentrations" of the analytes conform to the method and surrogate tables provided in this SOP. The lab can pre-spike the surrogates and spike compounds if client-specified to do so. As most drum/waste samples result in very high dilutions, it has been the labs experience that surrogates and Matrix Spikes are most often diluted out and provide no useful information. Unless otherwise assigned to do so, surrogate and matrix spiking will take place at time of analysis.

7.4 Preventive Maintenance

Instrumental maintenance can be categorized as daily and "as required".

7.4.1 Daily Maintenance

The most routinely performed maintenance includes:

- Purge-line or sample transfer line rinses within the concentrator and vial autosampler
- Analysis of blanks after high level samples
- GC oven bake after high level samples

7.4.2 "As Required"

Most maintenance is done on an "as needed" basis, is operator determined and can be categorized as GC, Concentrator, or MS related.

1. GC Related

- change column; condition new column
- clean separator; change separator
- check helium flow rate
- change gas cylinders and moisture trap

2. MS Related

- clean source/rods and anything associated with that activity

3. Concentrator Related

- change transfer line; clean transfer line
- replace trap; condition new trap
- refurbish Concentrator
- check purge pressure and flow rate
- analysis of position blanks after high-level samples
- change bulk head fitting

4. Autosampler Related

- change sparge needle
- change pencil filters
- flush standard pickups
- calibrate standard valve
- run vial position calibration
- clean transfer rods
- oil bearings

Required maintenance may be performed for a variety of reasons. Certain trouble-flags will indicate what maintenance procedures may be required. A description of the situation, actions taken and follow-up must be documented in the instrument maintenance database. An example of the maintenance database appears in Attachment 3.

7.5 Documentation/Tracking of Sample Analyses

1. The preparation and analysis is recorded in the GC/MS Volatiles Logbook (Attachment 3), and must be completed for each day's analysis. The book is set up to track the analysis of all the samples analyzed during the 12-hours, initial review and data crunching documentation for the samples in the batch, tune and standard information etc..

2. The GC/MS VOA lab employs several forms that serve both a tracking and review function. The Sample Tracking Sheet (BigBoard) is filled out for each job. It contains information the analyst needs as for method, QC requirements, special reporting requirements, screening results etc.., in addition for space to track the analysis of every single sample in the job and the outcome of that analysis.

3. In addition, all samples logged into the department appear on a hold-time summary sheet where ALL samples in-house are listed by hold-times and due dates. This summary is utilized by the analysts when making decisions as to methods and analyses that are needed for the day. As samples are analyzed and reviewed, the summary sheet is constantly updated to reflect those samples completely analyzed, those requiring dilutions and re-analyses (essentially a posted summary of the Sample Tracking Sheets). At the beginning of each day, the completed analyses are removed from the summary sheet by updating the analyzed samples into LabNet. The Sample Tracking Sheet and Tune Form can be found in Attachment 3.

7.5.1 Archival of Data

There are three full back-ups performed per week.

- Every Thursday a full back up of VOA data is performed.
- Every Friday a full back up of SVOA data is performed.
- Every Tuesday a system back up (minus the NBS Library) is performed. There are two tapes provided for this back up, and are rotated each week. Most current tapes are kept off site. Older tapes are in locked storage.

The system maintains a database, or logs, of each back-up session. Successful completion of each back-up can be verified each morning by accessing the job report logs in ARCServe. This is done each morning. Any missed jobs can be rescheduled and completed in the morning of the following day. As noted above, this database is re-archived after every normal back-up and can be retrieved at any time necessary.

7.5.2 Removal of Data

1. Although there is a substantial amount of space available to both BNA's and VOA's during busy periods the system can fill rather quickly. As an estimate, with a total of twelve (12) instruments, a maximum of about 2 months (per instrument) can be kept on the system at one time. There is not necessarily a set definite schedule of removing data from the system. As per laboratory SOP's, once the data package has been removed and all data associated from that batch has been reduced, reviewed, packaged and sent to report generation, the tune form is placed in designated location. Either by necessity or at the supervisor's discretion, these are compiled and the data then actually removed from the system.

2. The tune forms are then filed in the office area. Once a year, these forms are compiled and boxed and stored in a general data storage area.

8.0 QUALITY CONTROL

8.1 QC Summary

The department will review the quality controls as follows:

8.1.1 Method Blank (MB) / Laboratory Control Standard (LCS)

At least one MB and LCS will be included in each laboratory batch. Regardless of the matrix being processed, the LCS and MB will be in an aqueous media.

The MB will be examined to determine if contamination is being introduced in the laboratory. The LCS will be examined to determine accuracy and precision.

8.1.2 Accuracy

Accuracy will be measured by the percent recovery (%R) of the LCS. Method 8260B list or suggest accuracy limits for an initial demonstration of precision and accuracy. There are no further guidelines for spike recoveries. The current limits for the suggested spike compounds listed in the methods are listed in Attachment 2 of this SOP. The number of compounds being used for bench level control and the accuracy limits assigned to those compounds may vary with client, QAP, project etc.. This information is transmitted to the bench via the COC, kick-off meetings, tech profiles etc.., and indicated on one of the forms used at the bench. The accuracy limits are also posted on controlled boards in both the analytical and data areas (includes both method/sop limits and in-house generated limits. In-house generated limits are subject to change, but are included in Table 1).

8.1.3 Precision

Precision will be measured by the reproducibility of the LCS and will be calculated as Relative Percent Difference (RPD). The Methods list guidelines for the initial demo as noted above, but give no further guidelines for spike data. Current limits are listed in Table 1, however, RPD's are not used to assess bench level CA prior to sample analysis.

8.1.4 Surrogates

Surrogate Compounds will be added to every sample to measure performance of the analysis. Results must agree within statistical control limits in order to be considered acceptable. Limits are listed in Table 1. In-house surrogate limits are also generated as per method. As with LCS samples, the limits used to assess accuracy vary with client, QAP, project etc.., and the information transmitted to the bench in the same manner.

8.1.5 QC Charting

Precision and accuracy are monitored using LCS data. In-house criteria have been generated and are in use at present. Additional data may be added at QA/QC discretion during the year. During that period of time, additional LCSs will be logged into the system until adequate data are generated. Spike levels are 50 ppb/10 ppb for soils/waters. Only those compounds listed above are spiked and should be representative of the whole. The more non-routine compounds are not part of the spiking solutions. Other limitations (availability of second source) may also prevent adding these to spiking solutions. See comments in Section 6 for application of in-house control limits.

8.2 Corrective Actions

Listed below are the steps to be taken when an out-of-control situation occurs. The analyst must address the following issues as described below in the individual sections.

- demonstrate that all of the problems creating the out-of-control situation were addressed;
- document the problem and the action that was taken to correct the problem;
- document that an in-control situation has been achieved; and
- receive approval (signature) of the supervisor, section manager, QC personnel or other qualified personnel prior to release of data associated with the problem.

Bound corrective action (CA) logs are located in each run-log. In addition, a separate CA form, specific to a unique job, is attached to the COC and sample tracking form when the samples are initially entered into the sample tracking documentation used by the department. The log-book and sample # are used to note all out-of-control events, the actions taken to try and correct the problem, the return to control and qualification of data.

Discussed below are the suggested and required courses of action when an out-of-control situation has occurred.

8.2.1 BFB Criteria

If BFB criteria can not be met, determine if the source of the problem is instrumental or tune related. Inspect overall sensitivity, possible excessive background, the proportionality of the masses, relative abundances of the target masses. If it seems tune-related, adjust the tune parameters in Manual Tune slightly, until acceptance is achieved. If the problem seems instrumental, perform suggested trouble-shooting to locate and correct the problem (Suggestions can be found in most of the manuals). NO analysis can proceed until criteria are met. Corrective action for BFB analysis is documented in the CA logbook associated with the instrument in question. 'Return to control' must be documented.

8.2.2 Initial Calibration

If initial calibration can not be met, determine if the problem is analytical or instrumental. Some suggested questions to ask would be:

- were the standards prepared correctly?
- was the proper amount analyzed?
- check the chromatogram - did something happen on one or two analyses; i.e., a leak
- check the response factors - is one concentration level very high or low? re-analyze
- how old are the standards?

All calibration criteria must be met (Section 6.4). If the ICAL does not meet specified criteria, at minimum, the appropriate levels must be re-analyzed. If necessary, new standards should be prepared and the levels re-analyzed. During analysis of an initial calibration, documentation of the re-analyses of specific levels is not required. See previous section outlining CA for minimum COD values as well. Refer to the STL Corporate Policy, P-T-001, *Selection of Calibration Points* (Attachment 7), for further guidance.

8.2.3 Continuing Calibration

If continuing calibration can not be met, determine if the problem is analytical or instrumental. Some suggestions:

- check the chromatography
- is overall sensitivity low?
- excessive background?
- how old is the standard?
- need a new 5-point?
- has the tune shifted?

Compare the relative abundances of 69, 131 and 219 from that day's manual tune to those on the day the initial calibration was analyzed. Slight adjustments to the tune may bring the standard in. Certain compounds will help indicate what the problem is.

All calibration criteria must be met (Section 6.5). If the CCAL does not meet specified criteria, at minimum the standard should be re-analyzed. A new standard may be prepared and then re-analyzed. If necessary, a new ICAL must be run. All action taken for CCAL's must be recorded in the CAR logbook for that instrument. 'Return to control' must be documented.

8.2.4 Method Blank (MB)

If the MB is/appears to be contaminated, re-analyze it on a different position. If contamination is still present, the problem may be in one of the common elements, such as the trap, transfer line, port valve or column. Baking the trap/column and running

position blanks may be necessary. If contamination has occurred beyond that, and maintenance is required (i.e., replace trap) it is documented in the Maintenance Logbook. Corrective action and return to control for Method Blanks is recorded in the CAR logbook for the appropriate instrument. Under extenuating circumstances, if analysis continues, qualification must be made as to the positive hits above the EQL for the compounds in question. Any associated samples analyzed in the tune must be noted. Any samples containing positive hits must be noted. IF, the samples containing positive hits can not be re-analyzed (i.e., past hold-time), the positive hits are flagged with "B" and the situation and data noted and qualified in a case narrative.

8.2.5 Surrogates

All surrogate recoveries are calculated. If ANY surrogates are outside limits in the MB, it must be re-analyzed. Analyses CAN NOT proceed until an in-control situation is demonstrated. Re-analyze the blank. If surrogates are still out, the instrument may need to be re-tuned (BFB) and/or another calibration standard analyzed. If the problem persists, further maintenance action may be required (i.e., trap replacement, clean separator).

Before pursuing other measures, check to be sure that:

- calculations are correct
- concentrations of the surrogates in the spiking solution are correct
- the correct amount of ISS/SSS solution was added
- ISS/SSS areas are reasonable

If any surrogates in a sample are outside limits, check the above first. Any sample that has a surrogate out must be re-analyzed. The re-analysis can take the form of a dilution, if there is reasonable expectation that a high concentration of a target compound is causing a matrix effect. If the surrogate(s) is/are still outside limits, a matrix effect is demonstrated and both reports are submitted. Depending on the client, the best result may be reported and the other result narrated. If all surrogates are in-control on the re-analysis, only the second analysis is reported.

Every effort is made to complete the re-analysis within hold-time. If this is impossible (i.e. , capacity hold-times preclude re-analyses within hold-time), both reports may be submitted. This is documented in the narrative.

If the sample with the out-of-control surrogates is the same sample on which the MS and MSD has been performed, and the pattern is duplicated, then re-analysis is NOT required. Documentation of the similarities is required.

Surrogate corrective action is documented on the Individual CA Sample # Report for samples, and in the CAR logbooks for blanks and LCS samples.

8.2.6 Laboratory Control Sample (LCS)

As specified in Section 8.1.2, the number of compounds and the limits used to assess accuracy vary with client, QAP, project etc.. Both method/SOP and in-house generated limits are listed in the Appendices. The in-house limits are subject to change. The need and course of corrective action varies with the number of compounds being used for bench control and positive detected of compounds outside limits. The following guidelines are used :

(1) AFCEE : All compounds are used for bench control.

- If any compound exhibits low recoveries, the LCS is re-analyzed. If the compound is still low a new spike may be prepared and the LCS re-analyzed. Analysis should not continue until the situation is taken care of. All corrective action is documented at the time and return to control demonstrated for low compounds. IF, in extenuating circumstances, analysis is continued, the low compounds must be noted in the CAR book, associated samples must be qualified in the qualification section, absence of CA documented etc.. Data must be qualified for those compounds in the narrative.

- If any compound exhibits high recoveries, the LCS may be re-analyzed, and/or a new solution prepared, and/or a new standard prepared and calibrations repeated.

All corrective action is recorded at the time in the CAR logbook and return to control documented if applicable. AFCEE allows for high recoveries on a one time basis if the said compounds are not detected in the associated samples. Any high compounds must be noted in the CAR logbook, the associated samples listed in the qualification section, and the presence or absence of these compounds in the associated samples. If positive detects are noted, and the samples are unable to be re-analyzed, the situation must be documented and noted in the case narrative. Following the first occurrence of high recoveries, the bench will take appropriate note and follow-up with appropriate CA within a reasonable amount of time.

(2) QAP's etc.., specifying five compounds.

- ALL five compounds must be within limits for analysis to proceed. The LCS samples may be re-analyzed. New spike solutions may be prepared. Or new standards or CCAL's may be analyzed. All corrective action and return to control must be documented at the time in the CAR logbook of the appropriate instrument.

- The actual limits used for the five compounds may be QAP specific (usually those listed in the table in the appendix) or in-house generated by matrix and method. In either case, the above CA and required documentation apply.

- For all other compounds in the full-list spike, all recoveries are assessed, although no immediate corrective action may be required. If the recoveries are low, in general

another LCS may be re-analyzed. The spike solution and standard may be verified for correct concentrations. However, no corrective action is absolutely required by the bench unless an error is discovered. The recoveries may or may not be documented in the narrative, however, they are noted on the review form. The recoveries of the "un-controlled" compounds may be used for data interpretation.

- Although not strictly required to take immediate corrective action, the purpose of the full-spike is two-fold in that the bench should use it as an indicator of the status of the calibration standards, instrument conditions etc.., as well as a tool for data interpretation. Therefore, in keeping with good lab practice, the situation should be noted and assessed and any corrective action deemed necessary should be taken within a reasonable amount of time (Example: High recoveries on gases => new calibration standard may be needed).

8.2.7 Matrix Spikes (MS)

As specified in Section 8.1.2, the number of compounds and the limits used to assess accuracy vary with client, QAP, project, etc.. Both method/SOP and in-house generated limits are listed in the Appendices. The in-house limits are subject to change. The need and course of corrective action varies with the number of compounds being used for bench control and recoveries of same compounds in the associated LCS samples. The following guidelines are used :

(1) AFCEE : All compounds are used for bench level control.

- If the MS exhibits recoveries outside limits, AFCEE requires it to be re-analyzed as the MSD. No further action is required. Documentation is required however, on the individual CAR form and association made to the LCS for those compounds and in the case narrative. See above specifications for associated LCS samples.

(2) QAP's etc.., specifying 5 compounds.

- ALL 5 compounds are assessed. If recoveries are outside limits, the LCS is reviewed for those compounds. If the recoveries are within limits in the associated LCS samples, no further action is required. See above section concerning LCS CA for further information and action required for recoveries outside limits in LCS samples.

- The actual limits used for the five compounds may be QAP specific (usually those listed in the table in the appendix) or in-house generated by matrix and method. In either case, the above CA and required documentation apply.

- For all other compounds in the full-list spike, all recoveries are assessed, although no immediate corrective action may be required. The affected compounds may be compared to the same compounds in the associated LCS samples. See the above section for further information and action required for these compounds in the LCS

samples. The recoveries may or may not be documented in the narrative, however, they are noted on the review form. The recoveries of the "un-controlled" compounds may be used for data interpretation.

8.2.8 Internal Standard Policy

Method 8260 does not require re-analyses of samples for low internal standard areas. However, it is STL's policy to monitor areas and retention times, therefore, the following guidelines apply.

Situations requiring re-analyses :

- If ALL areas are outside limits the sample will be re-analyzed.
- Any sample that has a positive hit associated with any internal standard outside limits will be re-analyzed.
- If ANY surrogates are outside limits the sample will be re-analyzed.

Situations NOT requiring re-analyses :

- If all surrogates are within limits and there are no positive hits associated with those internal that are outside limits, the sample does not have to be re-analyzed. Situation should be addressed in the case narrative and noted on the sample CAR form.
- If all surrogates are within limits, but there is an obvious matrix effect occurring, even if positive hits are noted, the sample does not need to be re-analyzed. This decision will be approved by the supervisor or section manager. The situation must also be addressed on the sample CAR form and narrative.
- If there is historical evidence that shows a repeated pattern for a certain client and site, and this can be documented by reviewing past projects, the samples do not have to be re-analyzed. This decision will be approved by the supervisor or section manager.
- Internal standard areas for samples are documented on the Individual CAR form. Internal standard areas for CCAL to CCAL are documented in the appropriate CAR logbook.

Any sample showing retention times outside windows will be re-analyzed. This is documented in the appropriate manner as in the preceding paragraph.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Computer Data Production/Reduction

The Target 3.5 software produces a Total Ion Chromatogram (TIC), header, quant report and background subtracted spectra. For those clients requiring it, a 5 tentatively identified compound (TIC) search is also performed. The data system will produce an integration

listing and tentative identification of each hit found at the selected percentage of the largest peak present.

9.1.1 Quantitation of Target Compounds

Quantitation of the target compounds is performed by the data system can be accomplished as follows:

WATERs: concentration (mg/L) = $\frac{[A_x \times I_s]}{[A_{is} \times RF]} \times DF$

Where:
A_x = area of characteristic ion for target
I_s = concentration of internal standard (ng)
A_{is} = area of characteristic ion for int. std.
RF = response factor for target
DF = dilution factor (if any)

SOILs: concentration (mg/kg) = $\frac{[A_x \times I_s]}{[A_{is} \times RF \times D]} \times DF$

Where:
All variables are equal and
D = (100 - % moisture in sample/100) or 1 for wet weight. (As in the case of drum samples)

The target methods all contain calculations for waters and soils that allow automatic processing and calculations of concentrations to be completed. The user may enter some variables (Dilution Factor) and others are imported from LabNet. Sample prep info for VOA's is entered directly into LabNet. The sample volume is considered to be "constant" for calculation purposes. Less sample volume (in the case of waters) and soil weight (in the case of soils) are taken into account in the dilution factor entered by the user. For medium-level soils and waste/drum type samples medium level calculations are needed and actual weights are brought into LabNet.

NOTE: As noted previously, weights are recorded to 0.1 gram. It is SOP to weigh out 5.0 grams (or as appropriate for the dilution), however, to keep data entry and calculations simple. The same holds true for all water volumes.

9.1.2 Accuracy:

$$\%R = \frac{(A_T - A_0)}{A_F} \times 100$$

Where:
A_T = Total amount recovered in fortified sample
A_0 = Amount recovered in unfortified sample
A_F = Amount added to sample

9.1.3 Precision: $\%D = \frac{|B_1 - B_2|}{B_1} \times 100$

$$RPD = \frac{|B_1 - B_2|}{(B_1 + B_2)/2} \times 100$$

Where:
B_1 = %Recovery MS (or LCS)
B_2 = %Recovered MSD (or LCS)

9.1.4 Modifications for 8260B quantitation

1. Initial Calibration Criteria

Methods 8000B/8260B require the use of linear or higher order calibration curves for those compounds exceeding 15%.

The following equations apply :

Linear Regression: $y=a_0 + (1/a_1)x$ Quadratic Curve: $y = a_0 + (a1 * x) + (a2 * x^2)$

Power Curve: $y=e^{a0} * x^{(1/a1)}$

which is converted to : $\ln(y) = (1/a_1) * \ln(x) + a_0$

$x = Area_{UKN}/Area_{ISTD}$

$y= Amount_{UNK}/Amount_{ISTD}$

Once the $Amount_{UNK}$ is solved, the value is adjusted for total solids, dilution factors etc.., to calculate a final concentration.

The quantitation of compounds using either a linear regression, quadratic curve or a power curve as performed automatically by the Target software has been confirmed to be accurate.

Method 8000B/8260B specifies a minimum COD (R). The corrective action regarding an initial calibration for method 8260B as it relates to the 0.990 correlation coefficient acceptance criteria is outlined. When a compound has a correlation coefficient less than 0.990, the occurrence is documented by the analyst in the GC/MS VOA CAR section of the instrument's logbook. Any corrective action or data qualification is also documented in the CAR section of the logbook. All corrective actions taken may include those listed below.

Samples may be analyzed against an initial calibration that have compounds with a correlation coefficient less than 0.990 and the corrective actions taken may also include some but not all of the following:

- The data for these samples may be reported without qualification if the compounds with a correlation coefficient less than 0.990 are not detected in the sample, therefore no further corrective action is required.
- If a compound is detected in the sample that has a correlation coefficient less than 0.990, the samples may be reanalyzed against an initial calibration with an acceptable correlation coefficient and only the reanalysis will be reported on the sample. If this reanalysis occurs beyond analysis hold times then both analyses on the sample will be reported.
- If a compound is detected in the sample that has a correlation coefficient less than 0.990, the decision to reanalyze or to reported the data without further corrective action is made on a case by case basis with the approval of the supervisor, the section manager, the project manager and the client. The sample results may require qualification for this compound on the report and will be addressed in the case narrative.

2. Continuing Calibration Check

Prior to sample analysis a 10 ppb/ 50 ppb calibration check is completed. All minimum RF's must meet same limits. All CCC's must be less than 20% Drift as calculated below; the analysts may verify %DIFF and only calculate those that are close. (Error may only be made in favor of tighter control).

$$\%Drift = \frac{(Ci - Cc)}{Ci} \times 100$$

Where:
Ci = standard conc. (10/50)
Cc = measured conc. in cal check

9.1.5 Quantitation of TIC's (Tentatively Identified Compounds)

Quantitation of TIC's is performed by the Target processing software. The formulas above for waters and soils can be used with the following modifications. A_x and A_{is} should be taken from the total ion integration listing accompanying the TIC report produced by the data system. The nearest non-interfered with internal standard should be used. The RF is assumed to be one (1). The concentration is therefore an estimate and is flagged as such with a "J". Any TIC also found in the MB is flagged with a "JB". Any TIC identified with a CAS number is also flagged with an "N", indicating that the ID was based on the mass spectra. The operator should visually confirm that the integration is correct. If not, the peak in question must be manually integrated. The target system automatically calculates the actual concentration of the TIC's, including dilutions and total solids, once that information is retrieved from LabNet.

9.2 Operator Data Reduction/Review

The operator does on-screen review of all data and 1) makes judgments concerning the "realness" of those target compounds found and 2) makes judgments concerning the identification of the tentatively identified compounds and 3) modifies the output to produce a data package reflective of those decisions.

9.2.1 Initial Review

The GC/MS VOA area uses two kinds of corrective action documentation. The first consists of the CAR section of logbooks that are specific to each instrument. These logbooks contain sections to report out-of-control situations, CA, return-to-control and qualification sections for documenting problems related to general QC: tune, ICAL, CCAL, internal standard areas from CCAL to CCAL, and LCS samples. The second are the Individual CAR's that refer to a single job. These are used to record events, CA and final actions for surrogates, internal standard areas, carry-over situations, analyses past tune time, MS/MSD data etc.., for each sample in the batch. These forms are attached to the COC, along with the samples tracking sheets. Both may be used during initial review of the data. Examples of both can be found in Attachment 3. See Section 8.2 of this SOP for details on CA.

All data is initially reviewed on-screen. The review is both a QC review and a general review as described below.

- The MB contains no interferences or target compounds at the EQL.
- ALL surrogates are in control in the blank. Surrogate limits are listed in Table 1;
- ALL surrogates in samples are in control;
- LCS recoveries meet the limits listed in Table 1. See Section 8.2 concerning compounds and limits for LCS samples. In-house limits have been generated and are in use.
- Internal standard areas and retention times are checked and meet guidelines. Limits are listed in Attachment 2. Additional guidelines can be found in Section 8.2.
- The sample does not require any further dilutions or analysis at a more concentrated level. Dilutions are made to keep the target in the upper half of the calibration range. The MS and MSD are never diluted to get spiked or non-spiked compounds within range, as this would reduce the matrix affect assessment.
- Visually confirm complete integration for any large and/or saturated target compounds.
- The sample does not require re-analysis for any other reason (i.e., leak, analysis past tune time, ISTD areas low, etc..).

9.2.2 Identification of Targets

The following guidelines are used in the positive identification of target compounds.

1. "elution of component at the same relative retention time as the standard component."

The elution times should compare within +- 30 s. The standard must be run on the same 12 hour period as the sample. If co-eluting analytes interfere with the comparisons of retention times, other ions characteristic to that compound can be used to confirm relative retention times.

2. "correspondence of the sample component and standard component mass spectrum." Comparisons of sample spectra to standard spectra must be made using standard spectra obtained from the GC/MS system.
All ions present in the standard spectrum at a 10% relative intensity (most abundant ion being 100%) should be present in the sample.

The relative intensities of the above ions should agree within ±20%, between the standard and sample. If an ion is 50% intensity in the standard the corresponding ion must be between 30 and 70% in the sample.

Ions >10% in the sample but not present in the standard should be considered and accounted for. (A user program exists to aid in this).

3. **Operator judgment**. If a compound can not be verified by the above, but in the operators technical judgment the ID is correct, it is reported as such.

- Once all positive identification is made, the file is modified to reflect these decisions. At this time TIC's may also be reviewed and name. In each case where the file has been edited or manual integrations have taken place the operator must identify, initial and date the changes on the hardcopy.

9.2.3 Manual Integration Policy

In each case where the file has been edited or manual integrations have been performed the operator must identify, initial, and date the changes on the hardcopy report. The following guidelines apply:

- Manual integrations should be consistent between all files integrated.
- Manual integrations should not be performed to meet QC criteria.
- Manual integrations are automatically flagged with an 'M' on the raw data.
- Excessive manual integrations may reflect an instrumental or methodological problem that should be addressed.

- Manual integrations shall follow the STL Corporate SOP for Manual Integrations (S-Q-004 – Attachment 8). Example integrations and documentation are provided within this attachment.

Manual integrations are most often performed for the following reasons:

- Assignment of correct peak that was mis-identified by the data system.
- Incomplete auto-integration due to high level of target compound detected.
- Incomplete auto-integration due to background interference.
- Incorrect auto-integration due to co-elution or near co-elution of compounds.
- Missed peaks.

The analysts review all integrations. Spectra and Extracted Ion Chromatography Profiles (EICP) are printed after any integration takes place for target compounds and are routinely included in the data packages. If EICP's for internal standards, surrogates and calibration standards are required to satisfy client deliverables, they can be provided, but will not be routinely added. Manual integrations may be documented in the case narrative if so required, however, references to this SOP will be used for explanations, and any further documentation beyond initials and dates will not be done.

9.2.4 Identification of TIC's

In general, up to as many as 5 non-target compounds are tentatively identified by the data system and operator. Compounds with responses >10% of the nearest ISTD are identified. The data system provides the operator with a SUB ADC C sample spectrum, spectra of the first three matches and a listing of two other possibilities. Molecular formulas, molecular weights and CAS #'s are included. The following guidelines are used:

Relative intensities of major ions in the reference spectrum should be present in the sample (ions >10%).

- Relative ions should agree within ±20%;
- Molecular ions in the reference should be in the samples;
- Review the possibility of background and/or co-eluting compounds for those ions present in the sample but not in the standard;
- If ions are present in the sample but not in the standard, review the possibility of the presence of background or co-eluting compounds;
- If ions are present in the standard but not in the sample, review the possibility that the ions were subtracted out because they are also common to the background or co-eluting compounds;
- In the event no valid interpretation can be made, the compound is called "unknown".
- Interpretation can be often narrowed down to a class of compounds, molecular formula or weight.

9.3 Final Review

1. Once (a) the analysis is determined to be acceptable and (b) the initial review and data reduction has occurred (verifiable on the Tune Form) and (c) the analyst has entered sample prep info into LabNet, the following steps occur. The sample prep information, client ID information and some data applicable to fields in the forms is retrieved from LabNet. At this point, the analyst then usually prints hard-copies of all the necessary raw data. The analysts review the hard-copies and initial and date them, documenting that review.

2. All required forms are then generated using the Target software. Most, if not all of these steps, are documented on the tune form. The package is then assembled and ready for the first review.

3. Upon the first 100% review, the review form is initialed and dated as reviewed. The initial review is normally done by the analyst preparing the data package. The package, with its review sheet, comments and any CAR forms is submitted to the supervisor or section manager for a second review and validation. Once the data passes review in the department, it is submitted to report generation/QA/QC for appropriate follow-up action.

4. The complete analysis scheme can be summarized below (Section 7.1.1 & 7.1.2) and in Attachment 5. The entire sample tracking system can be summarized in Attachment 5. The Tune Form is used to verify many of these steps of review and data reduction.

10.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Waste from this procedure will enter the 'Flammable Vials' wastestream.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

Table 1. Estimated Quantitation Limits for Volatile Analytes; Laboratory Statistical Control Limits
Table 2. Characteristic Mass for Purgeable Organics Compounds

Figure 1. Example: Total Ion Chromatogram for 10 mL Purge Water
Figure 2. Example: Total Ion Chromatogram for 5 mL Purge Soil

Attachment 1. Example: Method Listings; Concentrator Conditions; Flow Settings
Attachment 2. Example: Target and Internal Standards; Surrogate Recovery Limits; LCS / MS Recovery Limits; Internal Standard Guidelines
Attachment 3. Example: GC/MS Volatiles/CAR Logbook; Sample Tracking Sheet; Maintenance Database
Attachment 4. Calibration Evaluation and Acceptance Criteria
Attachment 5. Example: Analysis and Sample Tracking Flowcharts
Attachment 6. Example: Data Review Form
Attachment 7. P-T-001: STL Corporate Policy for the Selection of Calibration Points
Attachment 8. S-Q-004: STL Corporate SOP for Manual Integrations

Appendix A. Requirements for DOD QSM Version 3.0

Historical File:

Revision 00: 06/22/92
Revision 01: 04/26/93
Revision 02: 05/26/93
Revision 03: 01/24/94
Revision 04: 07/15/94
Revision 05: 11/20/95
Revision 06: 04/09/96
Revision 07: 04/10/97
Revision 08: 06/13/97
Revision 09: 02/11/98
Revision 10: 01/29/99
Revision 11: 03/08/99
Revision 12: 09/28/00
Revision 13: 10/21/02
Revision 14: 06/28/04
Revision 15: 09/09/05

Reasons for Change, Revision 15:

- Annual review
- Addition of DOD QSM Version 3.0 Requirements and CAP

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Table 1.

Example: Estimated Quantitation Limits for Volatile Analytes[a] Laboratory Statistical Control Limits

[a]Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following example information for further guidance on matrix-dependent EQLs.

[b]EQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Method Limit Report using report code 8260B Volatile Organics (8260B)

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
1,1-Dichloroethane		ug/L	0.15	1.0	70	124	20		
1,1-Dichloroethene		ug/L	0.25	1.0	51	136	20		
1,1-Dichloropropene		ug/L	0.38	1.0	70	125	20		
1,2-Dichloroethane		ug/L	0.25	1.0	67	120	20		
1,2-Dichlorobenzene		ug/L	0.29	1.0	72	118	20		
1,2-Dichloroethane-d4 (surr)		ug/L						62	127
1,2-Dichloropropane		ug/L	0.19	1.0	76	116	20		
1,3,5-Trichlorobenzene		ug/L	0.64	1.0	72	143	20		
1,3-Butadiene		ug/L	0.24	1.0					
1,3-Dichlorobenzene		ug/L	0.21	1.0	71	120	20		
1,3-Dichloropropane		ug/L	0.22	1.0	72	118	20		
1,4-Dichlorobenzene		ug/L	0.25	1.0	70	118	20		
1-Chlorohexane		ug/L	0.20	1.0	57	124	20		
1,1,1-Trichloroethane		ug/L	0.17	1.0	70	127	20		
1,1,1,2-Tetrachloroethane		ug/L	0.33	1.0	77	120	20		
1,1,2-Trichloroethane		ug/L	0.24	1.0	63	127	20		
1,1,2,2-Tetrachloroethane		ug/L	0.34	1.0	61	122	20		
1,2-Dibromoethane (EDB)		ug/L	0.33	1.0	62	123	20		
1,2,3-Trichloropropane		ug/L	0.35	1.0	62	124	20		
1,2,3-Trichlorobenzene		ug/L	0.43	1.0	66	124	20		
1,2,4-Trichlorobenzene		ug/L	0.36	1.0	60	132	20		
1,2,4-Trimethylbenzene		ug/L	0.26	1.0	71	131	20		
1,2-Dichloroethene (total)		ug/L	0.34	1.0	72	129	20		
1,2-Dibromo-3-chloropropane		ug/L	0.41	1.0	57	119	20		
1,3,5-Trimethylbenzene		ug/L	0.18	1.0	70	132	20		
2,2-Dichloropropane		ug/L	0.17	1.0	68	127	20		
2-Butanone (MEK)		ug/L	1.0	5.0	29	139	20		
2-Chlorotoluene		ug/L	0.16	1.0	70	127	20		
2-Hexanone		ug/L	0.99	5.0	36	144	20		
2-Nitropropane		ug/L	17.	100.					
2-Chloroethylvinylether		ug/L	1.0	2.0	17	129	20		
2-Methylnaphthalene		ug/L	0.41	1.0					
3-Chloropropene (Allyl Chloride)		ug/L	1.1	2.5					
4-Chlorotoluene		ug/L	0.18	1.0	70	126	20		
4-Methyl-2-pentanone (MIBK)		ug/L	0.92	5.0	39	137	20		
Acetone		ug/L	1.4	5.0	14	177	20		
Acetonitrile		ug/L	5.6	40.					
Acrolein		ug/L	12.	200.					
Acrylonitrile		ug/L	2.0	40.					
Benzene		ug/L	0.23	1.0	75	122	20		
Bromobenzene		ug/L	0.22	1.0	76	118	20		
Bromochloromethane		ug/L	0.27	1.0	57	116	20		
Bromodichloromethane		ug/L	0.22	1.0	75	125	20		
4-Bromofluorobenzene (surr)		ug/L						67	132

Method Limit Report using report code 8260B Volatile Organics (8260B)

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
Bromoform		ug/L	0.32	1.0	65	115	20		
Bromomethane		ug/L	0.59	1.0	31	188	20		
Carbon disulfide		ug/L	0.15	5.0	21	111	20		
Carbon tetrachloride		ug/L	0.34	1.0	64	132	20		
Chlorobenzene		ug/L	0.15	1.0	76	116	20		
Chloroethane		ug/L	0.32	1.0	58	148	20		
Chloroform		ug/L	0.14	1.0	75	122	20		
Chloromethane		ug/L	0.20	1.0	31	182	20		
2-Chloro-1,3-butadiene (chloroprene)		ug/L	0.25	1.0					
Cyclohexane		ug/L	0.35	1.0					
Cyclohexanone		ug/L	23.	100.					
Dibromofluoromethane (surr)		ug/L						77	119
Dibromochloromethane		ug/L	0.22	1.0	73	116	20		
Dibromomethane		ug/L	0.21	1.0	68	116	20		
Dichlorodifluoromethane		ug/L	0.12	1.0	24	171	20		
Dichlorofluoromethane		ug/L	1.0	1.0					
Ethyl acetate		ug/L	2.6	10.					
Ethyl ether		ug/L	0.35	1.0	26	140	20		
Ethylbenzene		ug/L	0.21	1.0	75	125	20		
Ethylmethacrylate		ug/L	0.49	2.5					
Heptane		ug/L	0.31	1.0	10	157	20		
Hexachlorobutadiene		ug/L	0.36	1.0	63	145	20		
Hexane		ug/L	0.22	1.0	10	151	20		
Iodomethane		ug/L	0.58	2.5	24	173	20		
Isobutyl alcohol		ug/L	25.	100.					
Isopropyl ether		ug/L	0.25	1.0					
Isopropylbenzene		ug/L	0.20	1.0	64	119	20		
Methyl-tert-butyl-ether (MTBE)		ug/L	0.21	1.0	55	142	20		
Methacrylonitrile		ug/L	1.7	2.5					
Methyl acetate		ug/L	0.50	2.0					
Methyl cyclohexane		ug/L	0.30	1.0					
Methylene chloride		ug/L	0.24	1.0	64	127	20		
Methylmethacrylate		ug/L	0.85	2.5					
Naphthalene		ug/L	0.37	1.0	57	128	20		
Pentachloroethane		ug/L	0.68	2.5					
Propionitrile		ug/L	2.9	40.					
Styrene		ug/L	0.18	1.0	77	128	20		
tert-amyl methyl ether		ug/L							
tert-Butyl alcohol		ug/L							
Trihalomethanes (Total)		ug/L	1.0	1.0					
Tetrachloroethene		ug/L	0.18	1.0	70	125	20		
Tetrahydrofuran		ug/L	1.4	5.0	49	143	20		
Toluene		ug/L	0.18	1.0	77	120	20		
Toluene-d8 (surr)		ug/L						81	126

Method Limit Report using report code 8260B Volatile Organics (8260B)

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
Trichloroethene		ug/L	0.13	1.0	75	124	20		
Trichlorotrifluoroethane		ug/L	0.38	1.0	50	150	30		
Trichlorofluoromethane		ug/L	0.14	1.0	54	142	20		
Trimethylbenzene, Total		ug/L	0.26	1.0					
Vinyl acetate		ug/L	0.55	5.0	36	144	20		
Vinyl chloride		ug/L	0.16	1.0	52	134	20		
Xylenes (total)		ug/L	0.54	2.0	76	125	20		
bis(chloromethyl)ether		ug/L	2000.	2000.					
cis-1,4-Dichloro-2-butene		ug/L	2.5	2.5					
cis-1,2-Dichloroethene		ug/L	0.20	1.0	76	125	20		
cis-1,3-Dichloropropene		ug/L	0.15	1.0	72	115	20		
m&p-Xylenes		ug/L	0.36	2.0	75	123	20		
n-Butylbenzene		ug/L	0.35	1.0	64	142	20		
n-Propylbenzene		ug/L	0.16	1.0	69	132	20		
n-Butyl alcohol (1-Butanol)		ug/L	38.	100.					
o-Xylene		ug/L	0.19	1.0	76	121	20		
p-Isopropyltoluene		ug/L	0.29	1.0	66	130	20		
sec-Butylbenzene		ug/L	0.19	1.0	70	134	20		
trans-1,4-Dichloro-2-butene		ug/L	1.0	2.5					
tert-Butylbenzene		ug/L	0.16	1.0	70	133	20		
trans-1,2-Dichloroethene		ug/L	0.29	1.0	62	138	20		
trans-1,3-Dichloropropene		ug/L	0.16	1.0	68	119	20		
1,1-Dichloroethane		ug/L	0.15	1.0	70	124	20		
1,1-Dichloroethene		ug/L	0.25	1.0	51	136	20		
1,1-Dichloropropene		ug/L	0.38	1.0	70	125	20		
1,2-Dichloroethane		ug/L	0.25	1.0	67	120	20		
1,2-Dichlorobenzene		ug/L	0.29	1.0	72	118	20		
1,2-Dichloroethane-d4 (surr)		ug/L						62	127
1,2-Dichloropropane		ug/L	0.19	1.0	76	116	20		
1,3,5-Trichlorobenzene		ug/L	0.64	1.0	72	143	20		
1,3-Butadiene		ug/L	0.24	1.0					
1,3-Dichlorobenzene		ug/L	0.21	1.0	71	120	20		
1,3-Dichloropropane		ug/L	0.22	1.0	72	118	20		
1,4-Dichlorobenzene		ug/L	0.25	1.0	70	118	20		
1-Chlorohexane		ug/L	0.20	1.0	57	124	20		
1,1,1-Trichloroethane		ug/L	0.17	1.0	70	127	20		
1,1,1,2-Tetrachloroethane		ug/L	0.33	1.0	77	120	20		
1,1,2-Trichloroethane		ug/L	0.24	1.0	63	127	20		
1,1,2,2-Tetrachloroethane		ug/L	0.34	1.0	61	122	20		
1,2-Dibromoethane (EDB)		ug/L	0.33	1.0	62	123	20		
1,2,3-Trichloropropane		ug/L	0.35	1.0	62	124	20		
1,2,3-Trichlorobenzene		ug/L	0.43	1.0	66	124	20		
1,2,4-Trichlorobenzene		ug/L	0.36	1.0	60	132	20		
1,2,4-Trimethylbenzene		ug/L	0.26	1.0	71	131	20		

Method Limit Report using report code 8260B Volatile Organics (8260B)

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
1,1-Dichloroethane	Solid	ug/Kg	0.59	5.0	65	134	20		
1,1-Dichloroethene	Solid	ug/Kg	1.3	5.0	47	141	20		
1,1-Dichloropropene	Solid	ug/Kg	0.72	5.0	68	134	20		
1,2-Dichloroethane	Solid	ug/Kg	0.55	5.0	72	134	20		
1,2-Dichlorobenzene	Solid	ug/Kg	0.72	5.0	75	117	20		
1,2-Dichloroethane-d4 (surr)	Solid	ug/Kg						55	145
1,2-Dichloropropane	Solid	ug/Kg	0.55	5.0	76	124	20		
1,3,5-Trichlorobenzene	Solid	ug/Kg	2.3	5.0	78	134	20		
1,3-Butadiene	Solid	ug/Kg	2.0	5.0					
1,3-Dichlorobenzene	Solid	ug/Kg	0.72	5.0	71	120	20		
1,3-Dichloropropane	Solid	ug/Kg	0.61	5.0	81	123	20		
1,4-Dichlorobenzene	Solid	ug/Kg	0.70	5.0	72	120	20		
1-Chlorohexane	Solid	ug/Kg	0.70	5.0	52	126	20		
1,1,1-Trichloroethane	Solid	ug/Kg	0.72	5.0	71	137	20		
1,1,1,2-Tetrachloroethane	Solid	ug/Kg	0.60	5.0	78	126	20		
1,1,2-Trichloroethane	Solid	ug/Kg	0.82	5.0	79	133	20		
1,1,2,2-Tetrachloroethane	Solid	ug/Kg	0.62	5.0	73	125	20		
1,2-Dibromoethane (EDB)	Solid	ug/Kg	0.64	5.0	77	123	20		
1,2,3-Trichloropropane	Solid	ug/Kg	1.2	5.0	75	126	20		
1,2,3-Trichlorobenzene	Solid	ug/Kg	1.1	5.0	65	127	20		
1,2,4-Trichlorobenzene	Solid	ug/Kg	1.2	5.0	61	132	20		
1,2,4-Trimethylbenzene	Solid	ug/Kg	0.85	5.0	70	126	20		
1,2-Dichloroethene (total)	Solid	ug/Kg	1.3	5.0	69	134	20		
1,2-Dibromo-3-chloropropane	Solid	ug/Kg	1.5	5.0	61	133	20		
1,3,5-Trimethylbenzene	Solid	ug/Kg	0.81	5.0	68	125	20		
2,2-Dichloropropane	Solid	ug/Kg	1.4	5.0	70	134	20		
2-Butanone (MEK)	Solid	ug/Kg	2.2	5.0	41	166	30		
2-Chlorotoluene	Solid	ug/Kg	0.66	5.0	68	126	20		
2-Hexanone	Solid	ug/Kg	1.2	5.0	57	148	20		
2-Nitropropane	Solid	ug/Kg	180.	400.					
2-Chloroethylvinylether	Solid	ug/Kg	0.67	5.0	20	149	20		
2-Methylnaphthalene	Solid	ug/Kg	2.9	5.0					
3-Chloropropene (Allyl Chloride)	Solid	ug/Kg	4.3	10.0					
4-Chlorotoluene	Solid	ug/Kg	0.69	5.0	70	123	20		
4-Methyl-2-pentanone (MIBK)	Solid	ug/Kg	0.62	5.0	57	144	20		
Acetone	Solid	ug/Kg	3.2	5.0	50	176	20		
Acetonitrile	Solid	ug/Kg	15.	40.0					
Acrolein	Solid	ug/Kg	35.	200.					
Acrylonitrile	Solid	ug/Kg	7.1	40.0					
Benzene	Solid	ug/Kg	0.69	5.0	72	125	20		
Bromobenzene	Solid	ug/Kg	0.45	5.0	75	118	20		
Bromochloromethane	Solid	ug/Kg	0.75	5.0	61	122	20		
Bromodichloromethane	Solid	ug/Kg	0.57	5.0	82	131	20		
4-Bromofluorobenzene (surr)	Solid	ug/Kg						68	132

Method Limit Report using report code 8260B Volatile Organics (8260B)

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
Bromoform	Solid	ug/Kg	0.74	5.0	72	132	20		
Bromomethane	Solid	ug/Kg	2.7	5.0	39	165	20		
Carbon disulfide	Solid	ug/Kg	0.69	5.0	22	118	20		
Carbon tetrachloride	Solid	ug/Kg	0.73	5.0	67	130	20		
Chlorobenzene	Solid	ug/Kg	0.56	5.0	77	115	20		
Chloroethane	Solid	ug/Kg	3.1	5.0	56	145	20		
Chloroform	Solid	ug/Kg	0.68	5.0	73	135	20		
Chloromethane	Solid	ug/Kg	0.72	5.0	42	180	20		
2-Chloro-1,3-butadiene (chloroprene)	Solid	ug/Kg	2.5	5.0					
Cyclohexane	Solid	ug/Kg	2.4	5.0					
Cyclohexanone	Solid	ug/Kg	366.	400.					
Dibromofluoromethane (surr)	Solid	ug/Kg						63	146
Dibromochloromethane	Solid	ug/Kg	0.65	5.0	78	125	20		
Dibromomethane	Solid	ug/Kg	0.80	5.0	75	122	20		
Dichlorodifluoromethane	Solid	ug/Kg	0.86	5.0	39	159	20		
Dichlorofluoromethane	Solid	ug/Kg	0.63	1.0					
Ethyl acetate	Solid	ug/Kg	22.	50.0					
Ethyl ether	Solid	ug/Kg	2.2	5.0	29	125	30		
Ethylbenzene	Solid	ug/Kg	0.64	5.0	73	121	20		
Ethylmethacrylate	Solid	ug/Kg	3.4	10.					
Heptane	Solid	ug/Kg	2.4	5.0	20	130	30		
Hexachlorobutadiene	Solid	ug/Kg	2.6	5.0	50	154	20		
Hexane	Solid	ug/Kg	2.2	5.0	20	132	30		
Iodomethane	Solid	ug/Kg	3.6	10.0	34	189	30		
Isobutyl alcohol	Solid	ug/Kg	160.	400.					
Isopropyl ether	Solid	ug/Kg	2.4	5.0					
Isopropylbenzene	Solid	ug/Kg	0.68	5.0	59	114	20		
Methyl-tert-butyl-ether (MTBE)	Solid	ug/Kg	0.55	5.0	69	155	20		
Methacrylonitrile	Solid	ug/Kg	5.4	10.0					
Methyl acetate	Solid	ug/Kg	3.8	5.0					
Methyl cyclohexane	Solid	ug/Kg	2.4	5.0					
Methylene chloride	Solid	ug/Kg	1.6	5.0	67	133	20		
Methylmethacrylate	Solid	ug/Kg	8.0	10.					
Naphthalene	Solid	ug/Kg	1.0	5.0	54	133	20		
Pentachloroethane	Solid	ug/Kg	17.	20.					
Propionitrile	Solid	ug/Kg	9.5	40.0					
Styrene	Solid	ug/Kg	0.62	5.0	76	124	20		
tert-amyl methyl ether	Solid	ug/Kg		5.0					
tert-Butyl alcohol	Solid	ug/Kg		200.					
Trihalomethanes (Total)	Solid	ug/Kg							
Tetrachloroethene	Solid	ug/Kg	0.90	5.0	69	123	20		
Tetrahydrofuran	Solid	ug/Kg	1.5	5.0	22	159	20		
Toluene	Solid	ug/Kg	1.7	5.0	73	121	20		
Toluene-d8 (surr)	Solid	ug/Kg						66	140

Method Limit Report using report code 8260B Volatile Organics (8260B)

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
Trichloroethene	Solid	ug/Kg	0.66	5.0	74	124	20		
Trichlorotrifluoroethane	Solid	ug/Kg	1.2	5.0	50	150	30		
Trichlorofluoromethane	Solid	ug/Kg	0.95	5.0	57	136	20		
Vinyl acetate	Solid	ug/Kg	0.79	5.0	40	164	30		
Vinyl chloride	Solid	ug/Kg	0.70	5.0	49	144	20		
Xylenes (total)	Solid	ug/Kg	1.8	5.0	73	123	20		
bis(chloromethyl)ether	Solid	ug/Kg							
cis-1,4-Dichloro-2-butene	Solid	ug/Kg							
cis-1,2-Dichloroethene	Solid	ug/Kg	0.56	5.0	74	130	20		
cis-1,3-Dichloropropene	Solid	ug/Kg	0.58	5.0	78	118	20		
m&p-Xylenes	Solid	ug/Kg	1.2	10.0	73	122	20		
n-Butylbenzene	Solid	ug/Kg	1.1	5.0	64	133	20		
n-Propylbenzene	Solid	ug/Kg	0.74	5.0	66	126	20		
n-Butyl alcohol (1-Butanol)	Solid	ug/Kg	280.	400.					
o-Xylene	Solid	ug/Kg	0.62	5.0	75	120	20		
p-Isopropyltoluene	Solid	ug/Kg	0.82	5.0	65	121	20		
sec-Butylbenzene	Solid	ug/Kg	0.84	5.0	65	129	20		
trans-1,4-Dichloro-2-butene	Solid	ug/Kg	6.1	10.0					
tert-Butylbenzene	Solid	ug/Kg	0.78	5.0	67	124	20		
trans-1,2-Dichloroethene	Solid	ug/Kg	0.77	5.0	62	138	20		
trans-1,3-Dichloropropene	Solid	ug/Kg	0.60	5.0	77	127	20		

Method Limit Report using report code 8260B Volatile Organics (8260B)

Test Long Description	TMX	Units	MDL	RL	Limits LCSLL	Limits LCSUL	Limits LCSRPD	Limits SLL	Limits SUL
1,1-Dichloroethane	High/Me	ug/Kg	9.8	50.	68	119	30		
1,1-Dichloroethene	High/Me	ug/Kg	13.7	50.	44	143	30		
1,1-Dichloropropene	High/Me	ug/Kg	20.9	50.	65	134	30		
1,2-Dichloroethane	High/Me	ug/Kg	12.7	50.	64	115	30		
1,2-Dichlorobenzene	High/Me	ug/Kg	25.4	100.	76	125	30		
1,2-Dichloroethane-d4 (surr)	High/Me	ug/Kg						43	139
1,2-Dichloropropane	High/Me	ug/Kg	12.9	50.	70	122	30		
1,3,5-Trichlorobenzene	High/Me	ug/Kg	63.5	100.	65	113	30		
1,3-Butadiene	High/Me	ug/Kg	24.2	100.					
1,3-Dichlorobenzene	High/Me	ug/Kg	27.4	100.	75	119	30		
1,3-Dichloropropane	High/Me	ug/Kg	15.0	50.	71	118	30		
1,4-Dichlorobenzene	High/Me	ug/Kg	23.7	100.	76	127	30		
1-Chlorohexane	High/Me	ug/Kg	32.8	100.	63	133	30		
1,1,1-Trichloroethane	High/Me	ug/Kg	7.9	50.	69	133	30		
1,1,1,2-Tetrachloroethane	High/Me	ug/Kg	10.2	100.	74	120	30		
1,1,2-Trichloroethane	High/Me	ug/Kg	16.5	50.	67	133	30		
1,1,2,2-Tetrachloroethane	High/Me	ug/Kg	13.5	50.	70	126	30		
1,2-Dibromoethane (EDB)	High/Me	ug/Kg	66.5	100.	69	122	30		
1,2,3-Trichloropropane	High/Me	ug/Kg	23.4	100.	64	118	30		
1,2,3-Trichlorobenzene	High/Me	ug/Kg	49.2	100.	68	117	30		
1,2,4-Trichlorobenzene	High/Me	ug/Kg	64.4	100.	61	117	30		
1,2,4-Trimethylbenzene	High/Me	ug/Kg	24.7	100.	69	122	30		
1,2-Dichloroethene (total)	High/Me	ug/Kg	19.0	50.	60	139	30		
1,2-Dibromo-3-chloropropane	High/Me	ug/Kg	34.9	100.	56	102	30		
1,3,5-Trimethylbenzene	High/Me	ug/Kg	27.3	100.	66	125	30		
2,2-Dichloropropane	High/Me	ug/Kg	9.7	50.	41	131	30		
2-Butanone (MEK)	High/Me	ug/Kg	55.4	100.	40	125	30		
2-Chlorotoluene	High/Me	ug/Kg	24.6	50.	62	134	30		
2-Hexanone	High/Me	ug/Kg	61.5	100.	50	116	30		
2-Nitropropane	High/Me	ug/Kg	1650.	10000.					
2-Chloroethylvinylether	High/Me	ug/Kg	80.1	100.	10	100	30		
2-Methylnaphthalene	High/Me	ug/Kg	49.8	100.					
3-Chloropropene (Allyl Chloride)	High/Me	ug/Kg	109.	200.					
4-Chlorotoluene	High/Me	ug/Kg	32.1	50.	66	131	30		
4-Methyl-2-pentanone (MIBK)	High/Me	ug/Kg	63.5	100.	54	119	30		
Acetone	High/Me	ug/Kg	61.3	200.	34	143	30		
Acetonitrile	High/Me	ug/Kg	392.	800.					
Acrolein	High/Me	ug/Kg	974.	2000.					
Acrylonitrile	High/Me	ug/Kg	88.7	400.					
Benzene	High/Me	ug/Kg	4.4	25.	67	122	30		
Bromobenzene	High/Me	ug/Kg	15.6	100.	74	133	30		
Bromochloromethane	High/Me	ug/Kg	16.0	100.	60	124	30		
Bromodichloromethane	High/Me	ug/Kg	8.6	100.	66	128	30		
4-Bromofluorobenzene (surr)	High/Me	ug/Kg						57	124

Method Limit Report using report code 8260B Volatile Organics (8260B)

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
Bromoform	High/Me	ug/Kg	17.7	100.	70	123	30		
Bromomethane	High/Me	ug/Kg	48.4	100.	36	164	30		
Carbon disulfide	High/Me	ug/Kg	8.9	100.	21	124	30		
Carbon tetrachloride	High/Me	ug/Kg	29.3	50.	59	127	30		
Chlorobenzene	High/Me	ug/Kg	12.2	50.	80	125	30		
Chloroethane	High/Me	ug/Kg	19.2	100.	33	207	30		
Chloroform	High/Me	ug/Kg	9.8	50.	61	129	30		
Chloromethane	High/Me	ug/Kg	20.4	100.	55	129	30		
2-Chloro-1,3-butadiene (chloroprene)	High/Me	ug/Kg	24.8	100.					
Cyclohexane	High/Me	ug/Kg	35.3	100.					
Cyclohexanone	High/Me	ug/Kg	2330.	10000.					
Dibromofluoromethane (surr)	High/Me	ug/Kg						64	132
Dibromochloromethane	High/Me	ug/Kg	13.0	100.	70	119	30		
Dibromomethane	High/Me	ug/Kg	14.8	100.	67	121	30		
Dichlorodifluoromethane	High/Me	ug/Kg	22.3	100.	29	135	30		
Dichlorofluoromethane	High/Me	ug/Kg							
Ethyl acetate	High/Me	ug/Kg	258.	1000.					
Ethyl ether	High/Me	ug/Kg	34.6	100.	10	135	30		
Ethylbenzene	High/Me	ug/Kg	8.6	25.	78	128	30		
Ethylmethacrylate	High/Me	ug/Kg	48.7	200.					
Heptane	High/Me	ug/Kg	31.4	100.	10	119	30		
Hexachlorobutadiene	High/Me	ug/Kg	39.1	100.	63	126	30		
Hexane	High/Me	ug/Kg	22.2	100.	10	108	30		
Iodomethane	High/Me	ug/Kg	58.1	200.	50	150	30		
Isobutyl alcohol	High/Me	ug/Kg	2530.	10000.					
Isopropyl ether	High/Me	ug/Kg	25.5	100.					
Isopropylbenzene	High/Me	ug/Kg	20.5	100.	67	133	30		
Methyl-tert-butyl-ether (MTBE)	High/Me	ug/Kg	12.0	100.	47	126	30		
Methacrylonitrile	High/Me	ug/Kg	169.	200.					
Methyl acetate	High/Me	ug/Kg	50.2	100.					
Methyl cyclohexane	High/Me	ug/Kg	30.3	100.					
Methylene chloride	High/Me	ug/Kg	29.5	100.	57	129	30		
Methylmethacrylate	High/Me	ug/Kg	85.4	200.					
Naphthalene	High/Me	ug/Kg	35.9	100.	51	158	30		
Pentachloroethane	High/Me	ug/Kg	68.3	200.					
Propionitrile	High/Me	ug/Kg	222.	800.					
Styrene	High/Me	ug/Kg	16.0	50.	80	129	30		
tert-amyl methyl ether	High/Me	ug/Kg							
tert-Butyl alcohol	High/Me	ug/Kg							
Tetrachloroethene	High/Me	ug/Kg	19.3	50.	75	125	30		
Tetrahydrofuran	High/Me	ug/Kg	129.	200.	36	132	30		
Toluene	High/Me	ug/Kg	5.8	25.	72	123	30		
Toluene-d8 (surr)	High/Me	ug/Kg						70	128
Trichloroethene	High/Me	ug/Kg	10.9	25.	70	123	30		

Method Limit Report using report code 8260B Volatile Organics (8260B)

Test Long Description	TMX	Units	Limits MDL	RL	LCSLL	LCSUL	LCSRPD	SLL	SUL
Trichlorotrifluoroethane	High/Me	ug/Kg	33.1	100.	50	150	30		
Trichlorofluoromethane	High/Me	ug/Kg	16.8	100.	59	145	30		
Vinyl acetate	High/Me	ug/Kg	16.4	100.	54	144	30		
Vinyl chloride	High/Me	ug/Kg	12.6	25.	61	135	30		
Xylenes (total)	High/Me	ug/Kg	21.6	50.	77	131	30		
bis(chloromethyl)ether	High/Me	ug/Kg							
cis-1,2-Dichloroethene	High/Me	ug/Kg	13.8	50.	64	144	30		
cis-1,3-Dichloropropene	High/Me	ug/Kg	9.3	50.	68	123	30		
m&p-Xylenes	High/Me	ug/Kg	14.3	50.	76	133	30		
n-Butylbenzene	High/Me	ug/Kg	43.7	50.	64	118	30		
n-Propylbenzene	High/Me	ug/Kg	31.9	100.	69	130	30		
n-Butyl alcohol (1-Butanol)	High/Me	ug/Kg	3770.	10000.					
o-Xylene	High/Me	ug/Kg	7.1	25.	74	127	30		
p-Isopropyltoluene	High/Me	ug/Kg	33.4	100.	68	129	30		
sec-Butylbenzene	High/Me	ug/Kg	29.4	50.	69	139	30		
trans-1,4-Dichloro-2-butene	High/Me	ug/Kg	100.	200.					
tert-Butylbenzene	High/Me	ug/Kg	29.2	50.	71	125	30		
trans-1,2-Dichloroethene	High/Me	ug/Kg	9.8	50.	66	138	30		
trans-1,3-Dichloropropene	High/Me	ug/Kg	18.6	50.	60	115	30		

Table 2

Characteristic Mass (m/z) for Purgeable Organic Compounds

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion
Benzene	78	---
Bromobenzene	156	77,158
Bromochloromethane	128	49,130
Bromodichloromethane	83	85,127
Bromoform	173	175,254
Bromomethane	94	96
n-Butylbenzene	91	92,134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91,134
Carbon tetrachloride	117	119
Chlorobenzene	112	77,114
Chloroethane	64	66
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155,157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109,188
Dibromomethane	93	95,174
1,2-Dichlorobenzene	146	111,148
1,3-Dichlorobenzene	146	111,148
1,4-Dichlorobenzene	146	111,148
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65,83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61,63
cis-1,2-Dichloroethene	96	61,98
trans-1,2-Dichloroethene	96	61,98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110,77
Ethylbenzene	91	106
Hexachlorobutadiene	225	223,227
Isopropylbenzene	105	120
p-Isopropylbenzene	119	134, 91
Methylene chloride	84	86,49
Naphthalene	128	86, 49
n-Propylbenzene	91	120
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129,131,166

Table 2
(continued)
Characteristic Mass (m/z) for Purgeable Organic Compounds

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion
Toluene	92	91
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101,153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
Internal Std./Surrogates		
4-Bromofluorobenzene (S)	95	174, 176
1,4-Dichlorobenzene-d_4 (IS)	152	115, 150
Pentafluorobenzene (IS)	168	
Chlorobenzene-d_5 (IS)	117	
1,4-Difluorobenzene (IS)	114	
1,2-Dichloroethane-d_4 (S)	65	
Toluene-d_8 (S)	98	
Dibromofluoromethane (S)	113	

*NOTE: The primary and secondary ions listed here are taken directly from SW-846 Method 8260. The laboratory uses secondary ions in the cases of Ethylbenzene, Toluene, 1,1,2-Trichloroethane, Trichloroethene, 1,2,3-Trichloropropane and Xylenes due to interferences and/or to maintain consistency between methods.

Figure 1.

Example: Total Ion Chromatogram for 10 mL Purge Water

Data File: /var/chem/gcl16.i/090805.b/16c0908.d
Date : 08-SEP-2005 08:15
Client ID:
Sample Info: VSTD025
Purge Volume: 10.0
Column phase: Cap

Instrument: gcl16.i

Operator: JDN
Column diameter: 0.53

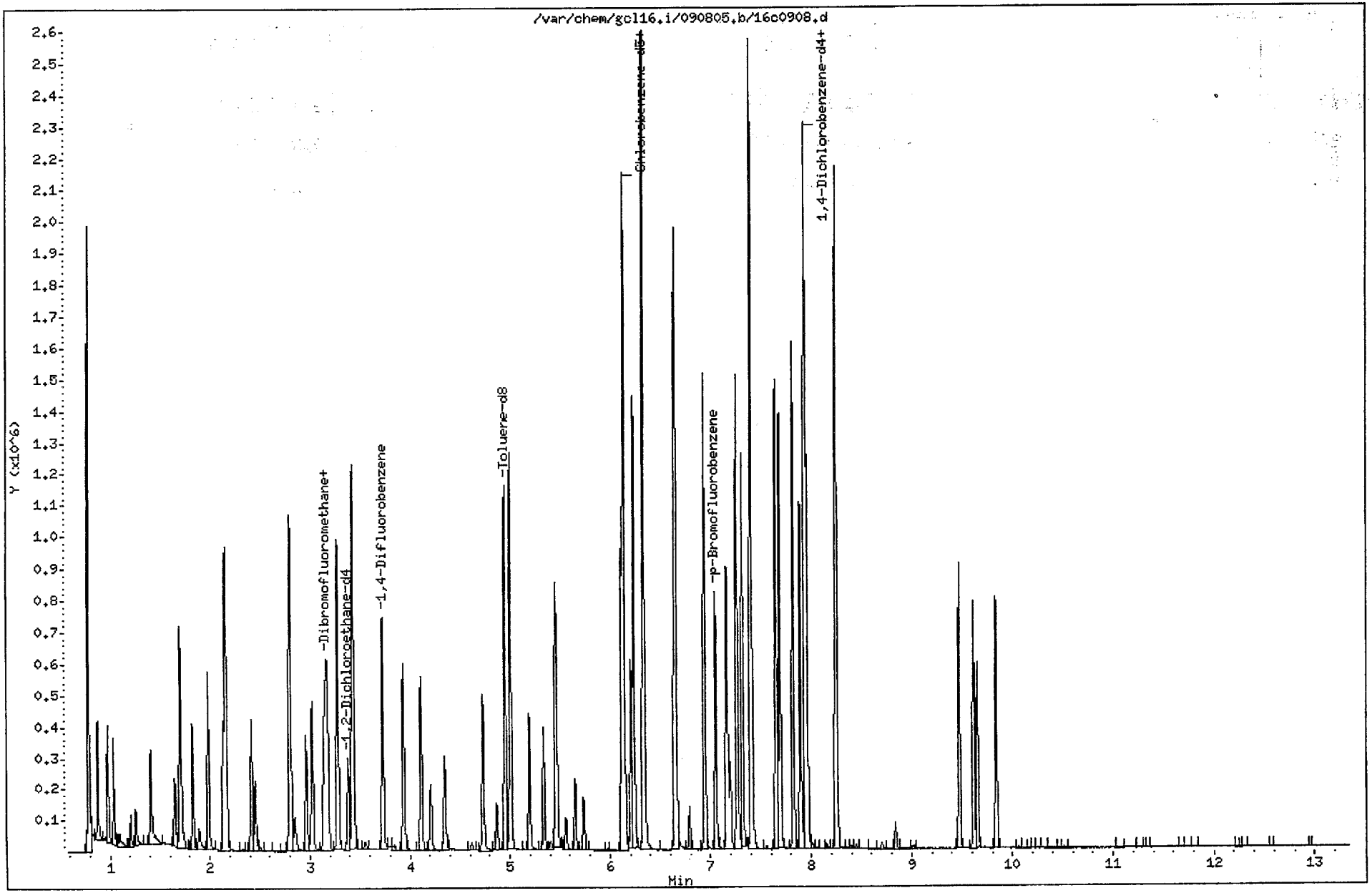


Figure 2.

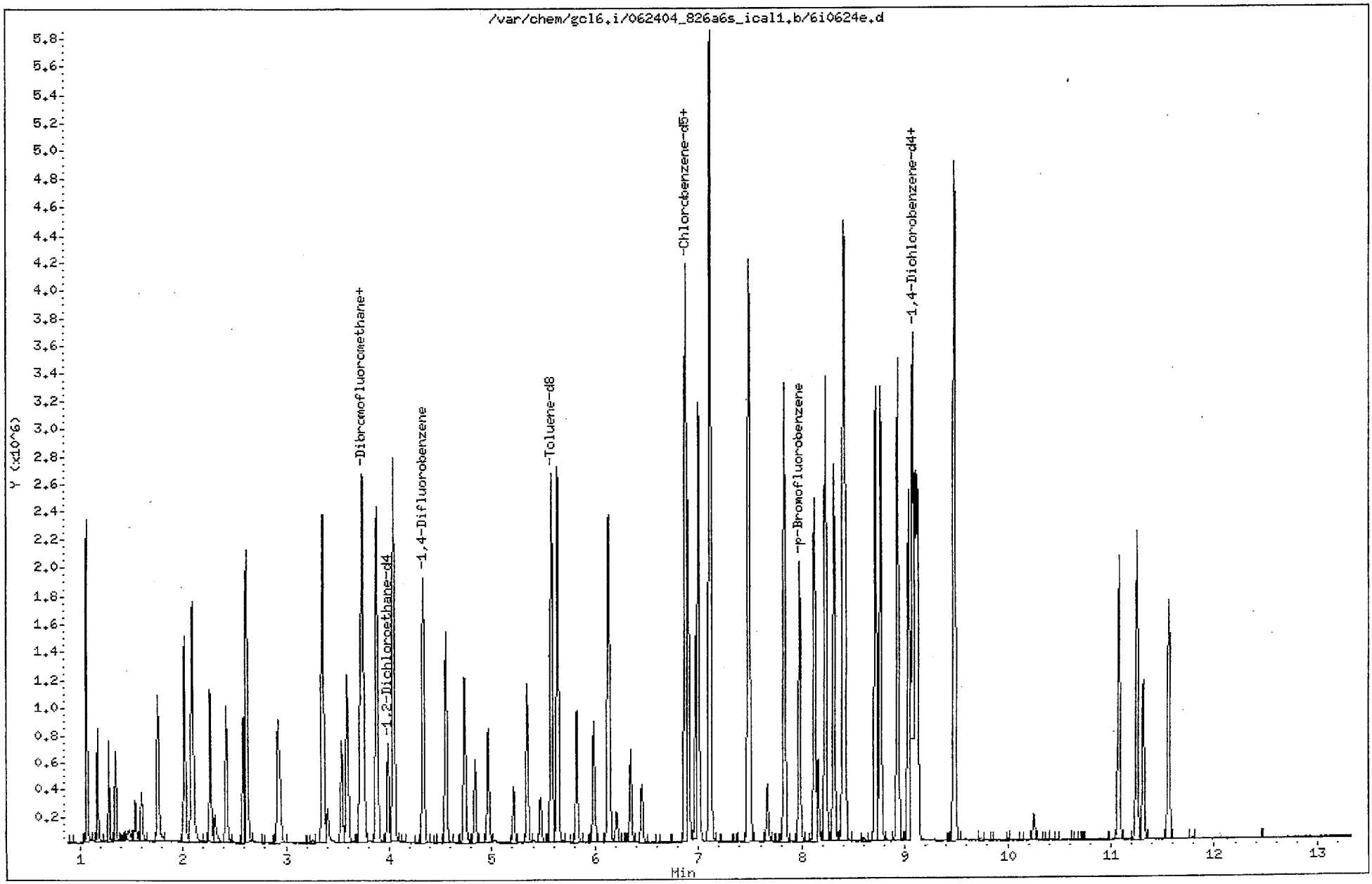
Example: Total Ion Chromatogram for 5 mL Purge Soil

Data File: /var/chem/gcl6.i/062404_826a6s_ical1.b/6i0624e.d
Date : 24-JUN-2004 13:14
Client ID: WSTD050
Sample Info: WSTD050

Instrument: gcl6.i

Operator: GES
Column diameter: 0.53

Column phase: Cap



Attachment 1.

Example: Method Listings; Concentrator Conditions; Flow Settings

Example: Volatiles Method for 5972

GC Oven Parameters

Initial Temperature = 40 °C
Initial Time = 2.0 minutes
Detector A Temperature = 180 °C
Detector B Temperature = 250 °C
Oven Equib. Time = 0.50 min.

Ramp Rate (°C/min.)	Final Temp. (°C)	Final Time (min.)
7.0	65	0.00
12.0	165	0.00
20.0	212	5.00

Run Time = 21.25 min.

Inlet Pressure Program

Gas = Helium
Column length = 75 m
Column Diameter = 0.530 mm
Initial Pressure = 3 psi
Rate (psi/min) = 0.00
Initial Time = 7.0 min.
Oven Temp. 50 °C
Program Time = 7.0 min.

Scan Parameters

Mass Range = 35-260
Threshold = 150
Scans/sec = 1.9
EM Voltage = 1938
Solvent Delay (scan start time): before the elution of the first compound.
Run Time (scan stop time): until after the elution of last compound.

Example: Volatiles Method for 5973

GC Oven Parameters

Initial Temperature = 50 °C
Initial Time = 2.0 minutes
Aux Temperature = 250 °C
Oven Equib. Time = 0.50 min.

Ramp Rate (°C/min.)	Final Temp. (°C)	Final Time (min.)
15.0	220	0.00

Run Time = 13.33 min.

Inlet Pressure Program

Mode=split
Gas = Helium
Column length = 25 m
Column Diameter = 0.25 mm
Constant flow = 1.0 mL/min
Injection port temp. = 250 °C
Program Time = 7.0 min.
Split ratio = 80:1
Gas saver = off

Scan Parameters

Mass Range = 35-260
Threshold = 100
Scans/sec = 6
EM Voltage = 1938
Solvent Delay = 0.8 min. (scan start time): before the elution of the first compound.
Run Time (scan stop time): until after the elution of last compound.

Concentrator Conditions

Trap Temp. Prior to Purge	< 35
Desorb Preheat	250
Desorb	250
Bake	260
Purge Time	11 min
Desorb	0.5 - 2 min (inst. dependent)
Bake Time	4 min

Trap = Vocarb 3000

Flow Conditions

Purge Pressure	20 psi
Purge Flow Rate	~40 mLs/min

Flow Adjustment

Capillary Column: 5972/MSD's;

· Make-up gas off/separator pump on: flow through separator is 5-10 mLs/minutes.

· Open make-up gas: adjust until you achieve ~30 mLs/minute through the separator. (On MSD's - adjust to 0.5 torr on gauge)

(Flow into the Mass Spec is ≤ 1 mL/minute)

Approximate Vacuums

~5 x 10^{-6} torr

Example Archon Conditions

Transfer Line Temp	110 deg C
Soil Valve	95 deg C
Purge Pressure	25 psi
Purge Flow	~ 40 ml/min
Purge Time	11 min
Desorb	0.5 -2 min
SamplePre-heat(soils)	40 deg C ~ 2 min

Attachment 2.

Example: Target and Internal Standards;
Surrogate Recovery Limits; LCS / MS Recovery Limits
Internal Standard Guidelines

Target and Internal Standards

Pentafluorobenzene
Acetone
Acrolein
Acrylonitrile
Bromochloromethane
Bromomethane
2-Butanone
Carbon disulfide
Chloroethane
Chloroform
Chloromethane
Dichlorodifluoromethane
1,1-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
2,2-Dichloropropane
Iodomethane
Methylene chloride
1,1,1-Trichloroethane
Trichlorofluoromethane
Vinyl acetate
Vinyl Chloride

Chlorobenzene-d_5
Bromoform
Bromofluorobenzene (surrogate)
Chlorodibromomethane
Chlorobenzene
1,3-Dichloropropane
Ethylbenzene
2-Hexanone
Styrene
1,1,1,2-Tetrachloroethane
Tetrachloroethene
Xylene

1,4-Difluorobenzene
Benzene
Bromodichloromethane
Carbon tetrachloride
2-Chloroethyl vinyl ether
1,2-Dibromoethane
Dibromomethane
1,2-Dichloroethane
1,2-Dichloroethane-d_4 (surrogate)
1,2-Dichloropropane
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
4-Methyl-2-pentanone
Toluene
Toluene-d_8 (surrogate)
1,1,2-Trichloroethane
Trichloroethene

1,4-Dichlorobenzene-d_4
Bromobenzene
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
2-Chlorotoluene
4-Chlorotoluene
1,2-Dibromo-3-chloropropane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobutadiene
Isopropyl benzene
p-Isopropyltoluene
Naphthalene
n-Propylbenzene
1,1,2,2-Tetrachloroethane
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

Surrogate Spike Recovery Default Limits

Surrogate Compound	Water	Low Soil	High Soil
Toluene-d_8	78-128	66-141	70-128
4-Bromofluorobenzene	73-122	60-140	57-124
1,2-Dichloroethane-d_4	61-131	50-145	43-139
Dibromofluoromethane	66-132	60-140	64-132

Note: Above are Surrogate Spike Recovery Default Limits from 8260B. These limits are for guidance only, not intended as set limits. In-house generated statistical limits or QAPP limits will be used whenever possible. See Table 1 for in-house generated statistical limits.

LCS / MS Recovery Default Limits

MS Compound	Water	Soil/Sediment
1,1-Dichloroethene	61-145	59-172
Trichloroethene	71-120	62-137
Chlorobenzene	75-130	60-133
Toluene	76-125	59-139
Benzene	76-127	66-142

Internal standard areas must be within -50% to 100% of the EICP for the corresponding continuing calibration standards. Internal standard retention times must not deviate by 30%.

Attachment 3.

Example: GC/MS Volatiles/CAR Logbook; Sample Tracking Sheet; Maintenance Database

STL Chicago
GC/MS Volatile Analysis Logbook

Instrument ID: 18

CHI-22-20-067/A-08/05

Target Batch(s): _____/_____ ICOC Initials_____Date_____Time: OUT_____IN_____

Time	Sample ID:	File:	#	Act	pH <2	I S	S S	SMP Wt/Vol	Inst. Dil	Misc. Info Must Include SRN's	Method	Prep Batch	Analytical Batch

Page: _____

Instrument ID: 18

CHI-22-20-067/A-08/05

Time	Sample ID:	File:	#	Act	pH <2	I S	S S	SMP Wt/Vol	Inst. Dil	Misc. Info Must Include SRN's	Method	Prep Batch	Analytical Batch

Corrective Actions:

Description Of Situation:	
Action Taken:	
Demonstration of Control:	

Analyst Signature: _____ Date: _____ Reviewer Signature: _____ Date: _____ Page: _____

rpjah

Job Analysis History

09/03/2005

V2

Surrogate Reagent...:

Method Code....: 8260B Volatile Organics
Job Number.....: 239672 Customer Job ID..: WASTE CHARACTERIZATI
Project Number.: 20004996 Remediation/Demolition Formosa Plastics

Holding Time.....: 13 Day HT
Customer.....: ATC Associates, Inc.
Proj. Cat..: INDUSTRIAL PM...: mannzr

Job Report Type...: p2
Contact.: Mark Kroenig
Hardcopy Due Date.: Fax Due Date.:

Sample #	QC	Client Sample ID	Matrix	HT Date	TAT Date	File Name	Dil	Tune name	Action	Analst	Prep Batch	Comments
1	N	083005-SOIL-1	SOIL	09/12/2005	09/14/2005							
2	N	083005-RESIN-1	SOLID	09/12/2005	09/14/2005							

Microsoft Excel - instrument tracker.xls

File Edit View Insert Format Tools Data Window Help

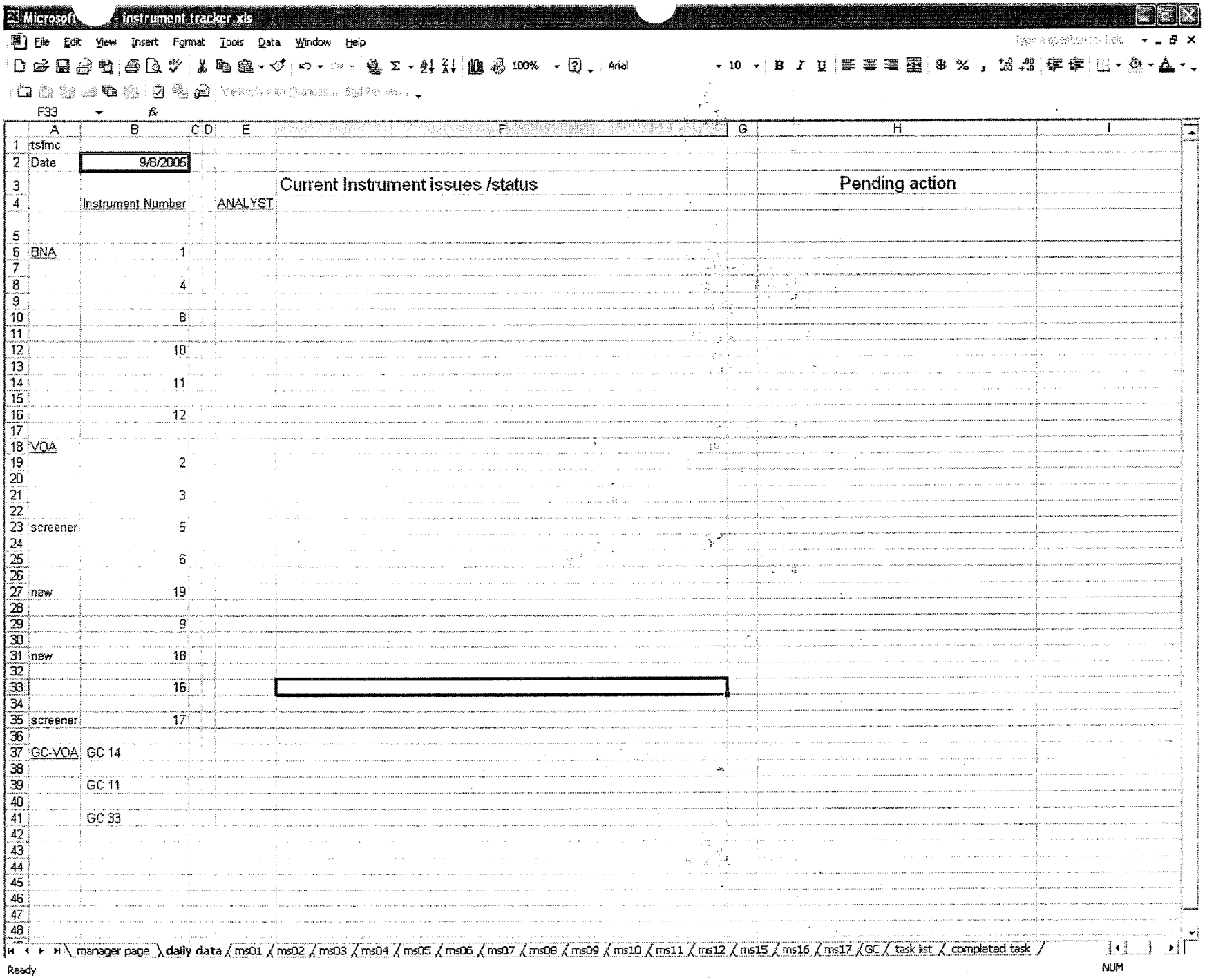
A4

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1														
2					Current Instrument issues /status		Pending action							
3		DATE		# ANALYST										
4		9/6/2005												
5		8/31/2005			manual is/ss curve.									
6		8/26/2005			Syringe not homed error, changed needle sparge probe									
7		8/25/2005												
8		8/17/2005			16C0821A lost with no reason, GC noted "Sample lost".									
9		8/16/2005												
10		8/15/2005												
11		8/10/2005												
12		8/9/2005												
13		8/8/2005												
14		8/3/2005			Change needle									
15		8/2/2005												
16		8/1/2005												
17		7/29/2005		ges	only working water instrument, standard home error sat.									
18		7/29/2005		ges	only working water instrument, standard home error sat.									
19		7/25/2005			John reset this AM -------- all seem to be running OK									
20		7/23/2005		ges	standard home error-lost 1/2 of a run.....just ran rest of samples.....John instrument and seems to be running OK		need to sonicate loop and make sure not over tight							
21		7/21/2005												
22		7/21/2005												
23		7/19/2005		JDN	Archon standard home error; It pulls back 5mls of water and then errors. I do not know if it is adding IS and it will not tell me. As ussual this is a random /F33problem.....7/20/5.....Same problem...									
24		7/18/2005												
25		7/15/2005												
26		7/15/2005												
27		7/13/2005												
28		7/12/2005			running									
29		7/11/2005		JDN	using lot of surr details tomorrow: samples									
30		7/8/2005			USED up all surrogate in 24 hour tune									
31		7/7/2005		JDN	no flow out of std 1 — changed vessels flow OK ran std ok runnning samp;es adding IS/ss from valve.									
32		6/29/2005												
33		6/28/2005												
34		6/23/2005												
35		1/0/1900												
36		6/21/2005												
37		6/20/2005												

manager page | daily data | ms01 | ms02 | ms03 | ms04 | ms05 | ms06 | ms07 | ms08 | ms09 | ms10 | ms11 | ms12 | ms15 | ms16 | ms17 | GC | task list | completed task

Ready

NUM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F33
tsfmc
Date 9/8/2005
Current Instrument issues /status
Pending action
Instrument Number
ANALYST
BNA 1
4
8
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11
12
VOA
2
3
screener 5
6
new 19
9
new 18
16
screener 17
GC-VOA GC 14
GC 11
GC 33
manager page daily data ms01 ms02 ms03 ms04 ms05 ms06 ms07 ms08 ms09 ms10 ms11 ms12 ms15 ms16 ms17 GC task list completed task
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Attachment 4.

Calibration Evaluation and Acceptance Criteria

INITIAL CALIBRATION DATA

Start Cal Date : 07-SEP-2005 10:57
End Cal Date : 07-SEP-2005 18:08
Quant Method : ISTD
Target Version : 3.50
Integrator : HP RTE
Method file : /var/chem/gcl16.i/090805.b/water16.m
Cal Date : 09-Sep-2005 08:04 nagelj

Calibration File Names:
Level 1: /var/chem/gcl16.i/090705_16ICAL1.b/16i907bb.d
Level 2: /var/chem/gcl16.i/090705_16ICAL1.b/16i907cc.d
Level 3: /var/chem/gcl16.i/090705_16ICAL1.b/16j0907f.d
Level 4: /var/chem/gcl16.i/090705_16ICAL1.b/16j0907e.d
Level 5: /var/chem/gcl16.i/090705_16ICAL1.b/16j0907d.d
Level 6: /var/chem/gcl16.i/090705_16ICAL1.b/16j0907c.d
Level 7: /var/chem/gcl16.i/090705_16ICAL1.b/16i907hh.d
Level 8: /var/chem/gcl16.i/090705_16ICAL1.b/16i907ii.d

Compound	0.5000 Level 1	1 Level 2	2 Level 3	10 Level 4	25 Level 5	50 Level 6	Curve	Coefficients b	m1	m2	%RSD or R^2
	75 Level 7	100 Level 8									
1 Dichlorodifluoromethane	+++++	6312	11265	42766	177096	363362					
	562212	757519					LINR	0.10908	0.69068		0.99521
2 Chloromethane	+++++	0.96321	0.66873	0.68144	0.85623	0.82397					
	0.79833	0.87196					AVRG		0.80912		12.98804
3 Vinyl chloride	+++++	0.68712	0.48418	0.49137	0.60080	0.57002					
	0.55336	0.60884					AVRG		0.57081		12.38629
4 1,3-Butadiene	+++++	0.65234	0.62054	0.63234	0.64964	0.65313					
	0.64261	0.61171					AVRG		0.63747		2.57547
5 Bromomethane	+++++	1513	2516	9987	27551	57864					
	93732	119135					LINR	0.07080	0.10919		0.99687

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Compound	0.5000 Level 1	1 Level 2	2 Level 3	10 Level 4	25 Level 5	50 Level 6	Curve	Coefficients b	m1	m2	%RSD or R^2	
	75 Level 7	100 Level 8										
7 Chloroethane	+++++	2962	5861	10644	57428	112935						
	215085	278376					QUAD	0.06741	5.18997	-1.36570	0.99276	
6 Dichlorofluoromethane	+++++	+++++	+++++	+++++	+++++	+++++						
	+++++	+++++					AVRG		0.000e+00		0.000e+00	<-
8 Trichlorofluoromethane	+++++	0.67663	0.48980	0.54846	0.64916	0.60506						
	0.62348	0.67850					AVRG		0.61016		11.41494	
9 Ethyl ether	+++++	0.27766	0.27746	0.28430	0.27589	0.27888						
	0.27690	0.26915					AVRG		0.27718		1.61356	
10 Acrolein	+++++	0.01266	0.01077	0.01115	0.01119	0.01067						
	0.01121	0.01164					AVRG		0.01133		5.91346	
11 1,1-Dichloroethene	+++++	0.37168	0.28264	0.28590	0.30622	0.29414						
	0.28213	0.31257					AVRG		0.30504		10.37555	
12 Trichlorotrifluoroethane	+++++	0.45852	0.33041	0.33474	0.35472	0.33951						
	0.32800	0.36091					AVRG		0.35811		12.83073	
13 Acetone	+++++	+++++	5439	11174	25472	51012						
	84095	106907					LINR	0.03223	0.09675		0.99398	
14 Iodomethane	+++++	0.37533	0.40040	0.41537	0.39714	0.42333						
	0.42402	0.40773					AVRG		0.40619		4.22374	

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Compound	0.5000 Level 1	1 Level 2	2 Level 3	10 Level 4	25 Level 5	50 Level 6	Curve	Coefficients b	m1	m2	%RSD or R^2	
	75 Level 7	100 Level 8										
15 Carbon Disulfide	+++++	+++++	0.98217	1.01062	1.16361	1.12290						
	1.08525	1.21783					AVRG		1.09706		8.20309	
16 Acetonitrile	+++++	7020	6347	24828	63399	124108						
	183798	228651					LINR	-0.30003	0.02590		0.99916	
17 3-Chloropropene	+++++	0.16894	0.17793	0.18588	0.17964	0.19007						
	0.18451	0.18824					AVRG		0.18217		3.99628	
18 Methyl acetate	+++++	3679	7036	22543	58962	122573						
	177521	308480					QUAD	-0.07251	6.08471	-2.04082	0.99660	
19 Methylene chloride	+++++	0.73942	0.54369	0.53443	0.54879	0.52556						
	0.52761	0.57581					AVRG		0.57076		13.36467	
20 Acrylonitrile	+++++	0.14591	0.10706	0.10739	0.10392	0.10082						
	0.10756	+++++					AVRG		0.11211		14.95409	
21 trans-1,2-Dichloroethene	0.65328	0.77519	0.53328	0.53852	0.56889	0.53848						
	0.53662	0.58479					AVRG		0.59113		14.31631	
22 Methyl-tert-Butyl Ether	+++++	1.32720	1.03875	1.09548	1.10734	1.08015						
	1.14258	1.23820					AVRG		1.14710		8.80601	
23 tert-Butyl alcohol	+++++	+++++	+++++	+++++	+++++	+++++						
	+++++	+++++					AVRG		0.000e+00		0.000e+00	<-

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	75 Level 7	100 Level 8										
24 Ethyl-tert-butyl Ether (ETBE)	+++++	+++++	+++++	+++++	+++++	+++++						
	+++++	+++++					AVRG		0.000e+00		0.000e+00	<-
25 Hexane	+++++	1.26491	1.20428	1.21671	1.16235	1.16360						
	1.16438	1.10971					AVRG		1.18371		4.19809	
26 1,1-Dichloroethane	1.32334	1.42497	1.06436	1.11257	1.16000	1.11874						
	1.13027	1.24423					AVRG		1.19731		10.31778	
27 Vinyl Acetate	+++++	12534	18415	81282	211746	471946						
	692874	984223					LINR	0.09325	0.87905		0.99245	
28 Isopropyl ether	+++++	2.22266	2.19299	2.34268	2.30073	2.32636						
	2.31802	2.23846					AVRG		2.27741		2.56608	
29 2-Chloro-1,3-butadiene	+++++	0.77650	0.80621	0.90131	0.92012	0.93853						
	0.92869	0.90707					AVRG		0.88263		7.26955	
30 2,2-Dichloropropane	0.81930	0.91310	0.72667	0.74119	0.79430	0.78553						
	0.79482	0.88197					AVRG		0.80711		7.91727	
31 cis-1,2-Dichloroethene	0.68289	0.73146	0.55477	0.56921	0.58775	0.56367						
	0.55926	0.61292					AVRG		0.60774		10.76551	
32 2-Butanone	+++++	+++++	0.23474	0.17323	0.18535	0.16882						
	0.19884	0.20831					AVRG		0.19488		12.61812	

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Compound	0.5000 Level 1	1 Level 2	2 Level 3	10 Level 4	25 Level 5	50 Level 6	Curve	Coefficients b	m1	m2	%RSD or R^2	
	75 Level 7	100 Level 8										
33 Propionitrile	+++++	0.03174	0.02568	0.02588	0.02567	0.02408						
	0.02629	0.02709					AVRG		0.02663		9.11851	
34 Ethyl Acetate	+++++	0.44137	0.36158	0.36328	0.34241	0.36967						
	0.37413	0.36873					AVRG		0.37445		8.33961	
36 Methacrylonitrile	+++++	0.20841	0.22298	0.23688	0.22895	0.25064						
	0.25924	0.26067					AVRG		0.23825		8.23345	
35 Bromochloromethane	+++++	0.29516	0.22782	0.22427	0.23739	0.22943						
	0.22989	0.25306					AVRG		0.24243		10.36402	
37 Tetrahydrofuran	+++++	+++++	0.09713	0.09433	0.09513	0.09546						
	0.10611	0.11687					AVRG		0.10084		8.89602	
38 Chloroform	1.08749	1.23519	0.89698	0.91498	0.94158	0.91382						
	0.92433	1.02029					AVRG		0.99184		11.88414	
40 1,1,1-Trichloroethane	0.84925	1.00580	0.72098	0.73999	0.79112	0.78376						
	0.78971	0.87843					AVRG		0.81988		11.10841	
42 2-Propanol	+++++	+++++	+++++	+++++	+++++	+++++						
	+++++	+++++					AVRG		0.000e+00		0.000e+00	<-
43 Cyclohexane	+++++	1.38370	1.52115	1.40124	1.32905	1.31832						
	1.30840	1.25337					AVRG		1.35932		6.36793	

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	75 Level 7	100 Level 8										
44 Carbon tetrachloride	0.38049	0.41386	0.32506	0.33248	0.36549	0.37386						
	0.38076	0.42226					AVRG		0.37428		9.14202	
45 1,1-Dichloropropene	0.88605	0.99199	0.74111	0.75931	0.79908	0.77804						
	0.77760	0.85186					AVRG		0.82313		10.14161	
47 Isobutanol	+++++	0.00981	0.01018	0.00992	0.00876	0.01052						
	0.01181	0.01170					AVRG		0.01038		10.39026	
48 Benzene	1.84403	1.93080	1.43094	1.41146	1.43566	1.36067						
	1.34810	1.45011					AVRG		1.52647		14.85766	
49 1,2-Dichloroethane	0.47492	0.51164	0.40776	0.40039	0.40404	0.38866						
	0.39858	0.42562					AVRG		0.42645		10.23738	
51 Heptane	+++++	0.77213	0.76816	0.83334	0.79029	0.80336						
	0.80832	0.77993					AVRG		0.79365		2.90839	
50 tert-Amyl-methyl ether (TAME)	+++++	+++++	+++++	+++++	+++++	+++++						
	+++++	+++++					AVRG		0.000e+00		0.000e+00	<-
53 Crotononitrile	+++++	+++++	+++++	+++++	+++++	+++++						
	+++++	+++++					AVRG		0.000e+00		0.000e+00	<-
54 n-Butanol	+++++	8813	17876	81678	187263	493908						
	850834	1134185					LINR	10.51859	0.00720		0.99371	<-

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Compound	0.5000 Level 1	1 Level 2	2 Level 3	10 Level 4	25 Level 5	50 Level 6	Curve	Coefficients b	m1	m2	%RSD or R^2	
	75 Level 7	100 Level 8										
55 Trichloroethene	0.41641	0.46733	0.33824	0.33233	0.34310	0.32881						
	0.33006	0.35379					AVRG		0.36376		13.94880	
56 Methyl cyclohexane	+++++	0.61669	0.62844	0.66951	0.65410	0.65303						
	0.64943	0.62996					AVRG		0.64302		2.86907	
57 1,2-Dichloropropane	+++++	0.48624	0.37162	0.36504	0.37656	0.36227						
	0.36779	0.39776					AVRG		0.38961		11.34641	
58 Dibromomethane	+++++	0.15446	0.13936	0.14001	0.14345	0.13939						
	0.14479	0.15570					AVRG		0.14531		4.81537	
59 Methylmethacrylate	+++++	0.16479	0.16964	0.20070	0.19942	0.22258						
	0.23140	0.23261					AVRG		0.20302		13.72324	
60 Bromodichloromethane	+++++	0.34585	0.28658	0.30993	0.33678	0.33630						
	0.34645	0.38540					AVRG		0.33533		9.24499	
61 Bis(chloromethyl)ether	+++++	+++++	+++++	+++++	+++++	+++++						
	+++++	+++++					AVRG		0.000e+00		0.000e+00	<-
62 2-Nitropropane	+++++	42001	102383	546710	1624201	4157364						
	6536544	8730227					LINR	8.51914	0.06460		0.99813	
63 2-Chloroethylvinylether	+++++	411	591	2671	9485	20167						
	37470	46972					QUAD	0.06552	49.13605	-107	0.99444	

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Compound	0.5000 Level 1	1 Level 2	2 Level 3	10 Level 4	25 Level 5	50 Level 6	Curve	Coefficients b	m1	m2	%RSD or R^2
	75 Level 7	100 Level 8									
64 cis-1,3-Dichloropropene	0.44135	0.49237	0.37511	0.42426	0.46633	0.47470					
	0.49326	0.53477					AVRG		0.46277		10.57682
65 4-Methyl-2-pentanone	+++++	+++++	0.16807	0.18744	0.20382	0.20089					
	0.23011	0.24814					AVRG		0.20641		13.99163
67 Toluene	1.17923	1.23667	0.92893	0.89172	0.91884	0.86863					
	0.86539	0.93023					AVRG		0.97745		14.86007
68 trans-1,3-Dichloropropene	0.32044	0.36306	0.29407	0.32830	0.36570	0.37837					
	0.39953	0.44013					AVRG		0.36120		12.92972
69 Ethylmethacrylate	+++++	9354	20039	96256	243885	573357					
	879828	1180286					LINR	0.10919	0.34451		0.99938
70 1,1,2-Trichloroethane	0.42035	0.42922	0.32688	0.33629	0.34645	0.33297					
	0.34724	0.38189					AVRG		0.36516		11.06832
71 Tetrachloroethene	6665	9133	17323	68629	169488	356615					
	507574	692973					LINR	0.01011	0.42442		0.99739
72 1,3-Dichloropropane	0.49993	0.54317	0.46747	0.46341	0.46856	0.45604					
	0.46926	0.50582					AVRG		0.48421		6.12927
73 2-Hexanone	+++++	+++++	3509	20726	55910	130455					
	228497	313007					QUAD	0.06543	6.90779	-2.47455	0.99888

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	75 Level 7	100 Level 8									
74 Dibromochloromethane	+++++	3589	7109	32624	89128	202909					
	317314	447798					LINR	0.12502	0.27723		0.99165
75 1,2-Dibromoethane	0.22129	0.21427	0.18937	0.19090	0.20070	0.19617					
	0.20744	0.22357					AVRG		0.20546		6.47781
77 Chlorobenzene	11458	25296	45484	183606	440815	911959					
	1284799	1744167					LINR	-0.00158	1.06917		0.99769
78 1-Chlorohexane	+++++	0.89859	0.75937	0.76872	0.83540	0.80226					
	0.78458	0.85081					AVRG		0.81425		6.14183
79 1,1,1,2-Tetrachloroethane	+++++	0.35462	0.27461	0.28982	0.32076	0.32049					
	0.32400	0.36555					AVRG		0.32141		10.03943
80 Ethylbenzene	0.78049	0.85065	0.63111	0.62986	0.66716	0.63878					
	0.61862	0.67848					AVRG		0.68689		12.22729
81 p,m-Xylene	1.79146	1.96499	1.51714	1.50072	1.58272	1.49437					
	1.42798	1.55255					AVRG		1.60399		11.29519
82 o-Xylene	1.70663	1.96365	1.41632	1.46797	1.55601	1.48848					
	1.43551	1.58026					AVRG		1.57685		11.55306
83 Styrene	1.02364	1.27405	0.98716	1.13799	1.26826	1.22328					
	1.18989	1.30381					AVRG		1.17601		10.02060

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		75 Level 7	100 Level 8										
	84 Bromoform	+++++	1839	3549	16345	45472	109713						
		177460	255265					QUAD	0.03005	8.80401	-4.09687	0.99984	<-
	85 Isopropylbenzene	+++++	4.51712	3.36501	3.57971	3.97131	3.88352						
		3.85957	4.35560					AVRG		3.93312		10.25719	
	86 Cyclohexanone	+++++	0.06376	0.06689	0.05930	0.02781	0.05933						
		0.07082	0.06605					AVRG		0.05914		24.37880	<-
	87 cis-1,4-Dichloro-2-butene	+++++	+++++	+++++	+++++	+++++	+++++						
		+++++	+++++					AVRG		0.000e+00		0.000e+00	<-
	89 Bromobenzene	+++++	1.07829	0.79946	0.80302	0.86433	0.83715						
		0.84049	0.95410					AVRG		0.88241		11.41019	
	90 1,1,2,2-Tetrachloroethane	0.62779	0.66071	0.50947	0.51576	0.54850	0.53304						
		0.57391	0.64095					AVRG		0.57627		10.31588	
	91 1,2,3-Trichloropropane	+++++	0.19345	0.16064	0.15628	0.16594	0.15859						
		0.17239	0.19277					AVRG		0.17144		9.16864	
	92 trans-1,4-Dichloro-2-butene	+++++	715	1699	6876	19126	49999						
		80564	+++++					LINR	0.21099	0.06371		0.99420	
M	93 Xylene (total)	1.70663	1.96365	1.41632	1.46797	1.55601	1.48848						
		1.43551	1.58026					AVRG		1.57685		11.55306	

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	75 Level 7	100 Level 8									
94 n-Propylbenzene	4.89333	5.26189	4.11450	4.29670	4.77239	4.65204					
	4.64444	5.21876					AVRG		4.73175		8.49205
95 2-Chlorotoluene	3.14549	3.47573	2.53737	2.58716	2.74141	2.69805					
	2.67699	3.04113					AVRG		2.86291		11.40037
96 4-Chlorotoluene	3.31841	3.84125	2.86885	2.89323	3.16110	3.01898					
	2.96802	3.32466					AVRG		3.17431		10.15482
97 1,3,5-Trimethylbenzene	3.28513	3.89642	2.92220	3.07135	3.34078	3.23269					
	3.15258	3.52489					AVRG		3.30325		9.07737
M 98 1,2-Dichloroethene (total)	0.66809	0.75332	0.54402	0.55387	0.57832	0.55108					
	0.54794	0.59886					AVRG		0.59944		12.44869
99 tert-Butylbenzene	3.41103	3.41459	2.41669	2.60278	2.85596	2.81310					
	2.76404	3.10530					AVRG		2.92293		12.36107
100 Pentachloroethane	+++++	5497	11547	57390	146885	328058					
	+++++	+++++					LINR	0.06691	0.19355		0.99911
101 1,2,4-Trimethylbenzene	3.57672	4.07780	3.04059	3.12226	3.42572	3.31008					
	3.28963	3.72236					AVRG		3.44564		9.84273
102 sec-Butylbenzene	4.27011	5.21162	3.88005	4.07317	4.45074	4.41824					
	4.35783	4.88699					AVRG		4.44360		9.62100

INITIAL CALIBRATION DATA

Start Cal Date : 07-SEP-2005 10:57
End Cal Date : 07-SEP-2005 18:08
Quant Method : ISTD
Target Version : 3.50
Integrator : HP RTE
Method file : /var/chem/gcl16.i/090805.b/water16.m
Cal Date : 09-Sep-2005 08:04 nagelj

Compound	0.5000 Level 1	1 Level 2	2 Level 3	10 Level 4	25 Level 5	50 Level 6	Curve	Coefficients b	m1	m2	%RSD or R^2
	75 Level 7	100 Level 8									
103 1,3-Dichlorobenzene	+++++	2.37869	1.65852	1.65718	1.79713	1.73913					
	1.72704	1.96736					AVRG		1.84644		13.93544
105 p-Isopropyltoluene	+++++	4.02598	3.10262	3.30196	3.66534	3.61026					
	3.53790	3.96306					AVRG		3.60102		9.19423
106 1,4-Dichlorobenzene	+++++	21651	36962	144920	358154	751309					
	1064041	1477614					LINR	0.05423	1.90017		0.99344
107 1,2-Dichlorobenzene	+++++	18415	31047	124544	304341	635821					
	894469	1225930					LINR	0.04064	1.57901		0.99486
108 n-Butylbenzene	3.47036	3.52839	2.84882	3.00831	3.42786	3.38796					
	3.32732	3.70394					AVRG		3.33787		8.36985
109 1,2-Dibromo-3-Chloropropane	+++++	749	1297	5670	14320	33479					
	54351	74991					QUAD	0.01507	14.21703	-10.64798	0.99973
110 1,3,5-Trichlorobenzene	+++++	1.20099	1.16837	1.27207	1.23243	1.20582					
	1.20528	1.17195					AVRG		1.20813		2.95215
111 1,2,4-Trichlorobenzene	+++++	1.31317	0.92653	0.92756	1.07752	1.05727					
	1.05126	1.17933					AVRG		1.07609		12.71172
112 Hexachlorobutadiene	+++++	0.78119	0.60511	0.58392	0.62827	0.64232					
	0.63740	0.70594					AVRG		0.65488		10.28997

INITIAL CALIBRATION DATA

Start Cal Date : 07-SEP-2005 10:57
End Cal Date : 07-SEP-2005 18:08
Quant Method : ISTD
Target Version : 3.50
Integrator : HP RTE
Method file : /var/chem/gc116.i/090805.b/water16.m
Cal Date : 09-Sep-2005 08:04 nagelj

Compound	0.5000 Level 1	1 Level 2	2 Level 3	10 Level 4	25 Level 5	50 Level 6	Curve	Coefficients b	m1	m2	%RSD or R^2
	75 Level 7	100 Level 8									
113 Naphthalene	+++++	19174	31106	137606	339533	756454					
	1145231	1587381					LINR	0.10862	2.05955		0.99125
114 1,2,3-Trichlorobenzene	+++++	11553	17282	71750	183927	394745					
	564296	777638					LINR	0.06638	1.00492		0.99405
115 2-Methylnaphthalene	+++++	5320	13073	68360	201777	458695					
	694147	927191					LINR	0.05055	1.09439		0.99960
$ 39 Dibromofluoromethane	+++++	+++++	0.49223	0.45466	0.44141	0.43718					
	0.45557	0.48212					AVRG		0.46053		4.79770
$ 46 1,2-Dichloroethane-d4	+++++	+++++	0.33492	0.30371	0.28823	0.28303					
	0.30004	0.31208					AVRG		0.30367		6.11627
$ 66 Toluene-d8	+++++	+++++	1.11696	1.13463	1.12158	1.11019					
	1.14428	1.18656					AVRG		1.13570		2.44757
$ 88 p-Bromofluorobenzene	+++++	+++++	0.51528	0.48144	0.47871	0.48588					
	0.49387	0.53014					AVRG		0.49755		4.15824

INITIAL CALIBRATION DATA

Start Cal Date : 07-SEP-2005 10:57
End Cal Date : 07-SEP-2005 18:08
Quant Method : ISTD
Target Version : 3.50
Integrator : HP RTE
Method file : /var/chem/gcl16.i/090805.b/water16.m
Cal Date : 09-Sep-2005 08:04 nagelj

Average %RSD Results.
Calculated Average %RSD = 10.5157089
Maximun Average %RSD = 15
* Passed Average %RSD Test.

Curve	Formula	Units
Averaged	Amt = Rsp/m1	Response
Linear	Amt = b + Rsp/m1	Response
Quad	Amt = b + m1*Rsp + m2*Rsp^2	Response

RECOVERY REPORT

Client Name: Client SDG: 090705
Sample Matrix: LIQUID Fraction: VOA
Lab Smp Id: ICAL SPIKE
Level: LOW Operator: JDN
Data Type: MS DATA SampleType: BS
SpikeList File: ICALSPK.spk Quant Type: ISTD
Sublist File: all.sub
Method File: /var/chem/gcl16.i/090705.b/water16.m
Misc Info: ICAL SPIKE,1,9,WATER16.m,090705.b

SPIKE	COMPOUND	CONC ADDED ug/L	CONC RECOVERED ug/L	% RECOVERED	LIMITS
1	Dichlorodifluorome	25.000	23.850	95.40	75-125
2	Chloromethane	25.000	28.677	114.71	75-125
3	Vinyl chloride	25.000	23.219	92.88	75-125
9	Ethyl ether	25.000	19.185	76.74	75-125
5	Bromomethane	25.000	27.558	110.23	75-125
7	Chloroethane	25.000	16.035	64.14*	75-125
14	Iodomethane	25.000	23.464	93.86	75-125
8	Trichlorofluoromet	25.000	23.320	93.28	75-125
11	1,1-Dichloroethene	25.000	28.154	112.61	75-125
13	Acetone	25.000	23.647	94.59	75-125
25	Hexane	25.000	14.439	57.76*	75-125
12	Trichlorotrifluoro	25.000	14.746	58.98*	75-125
15	Carbon Disulfide	25.000	17.163	68.65*	75-125
19	Methylene chloride	25.000	28.587	114.35	75-125
22	Methyl-tert-Butyl	25.000	29.170	116.68	75-125
21	trans-1,2-Dichloro	25.000	28.526	114.10	75-125
26	1,1-Dichloroethane	25.000	27.557	110.23	75-125
27	Vinyl Acetate	25.000	22.340	89.36	75-125
32	2-Butanone	25.000	23.962	95.85	75-125
31	cis-1,2-Dichloroet	25.000	28.258	113.03	75-125
30	2,2-Dichloropropan	25.000	25.452	101.81	75-125
51	Heptane	25.000	18.570	74.28*	75-125
35	Bromochloromethane	25.000	27.854	111.41	75-125
37	Tetrahydrofuran	25.000	29.360	117.44	75-125
38	Chloroform	25.000	26.379	105.52	75-125
40	1,1,1-Trichloroeth	25.000	27.495	109.98	75-125
45	1,1-Dichloropropen	25.000	27.455	109.82	75-125
44	Carbon tetrachlori	25.000	27.768	111.07	75-125
49	1,2-Dichloroethane	25.000	25.282	101.13	75-125
48	Benzene	25.000	26.025	104.10	75-125
55	Trichloroethene	25.000	25.608	102.43	75-125
57	1,2-Dichloropropan	25.000	25.769	103.07	75-125
58	Dibromomethane	25.000	26.560	106.24	75-125

	SPIKE	COMPOUND	CONC ADDED ug/L	CONC RECOVERED ug/L	% RECOVERED	LIMITS
	60	Bromodichlorometha	25.000	27.836	111.35	75-125
	63	2-Chloroethylvinyl	25.000	28.876	115.51	75-125
	64	cis-1,3-Dichloropr	25.000	25.145	100.58	75-125
	65	4-Methyl-2-pentano	25.000	26.892	107.57	75-125
	67	Toluene	25.000	24.127	96.51	75-125
	68	trans-1,3-Dichloro	25.000	23.412	93.65	75-125
	70	1,1,2-Trichloroeth	25.000	25.594	102.38	75-125
	72	1,3-Dichloropropan	25.000	26.224	104.90	75-125
	71	Tetrachloroethene	25.000	25.430	101.72	75-125
	73	2-Hexanone	25.000	28.088	112.35	75-125
	74	Dibromochlorometha	25.000	24.948	99.79	75-125
	75	1,2-Dibromoethane	25.000	25.111	100.44	75-125
	78	1-Chlorohexane	25.000	22.378	89.51	75-125
	77	Chlorobenzene	25.000	26.149	104.60	75-125
	79	1,1,1,2-Tetrachlor	25.000	26.048	104.19	75-125
	80	Ethylbenzene	25.000	24.044	96.17	75-125
	81	p,m-Xylene	50.000	47.828	95.66	75-125
	82	o-Xylene	25.000	24.199	96.80	75-125
	83	Styrene	25.000	26.627	106.51	75-125
	84	Bromoform	25.000	27.053	108.21	75-125
	85	Isopropylbenzene	25.000	22.459	89.83	75-125
	90	1,1,2,2-Tetrachlor	25.000	25.907	103.63	75-125
	91	1,2,3-Trichloropro	25.000	26.047	104.19	75-125
	89	Bromobenzene	25.000	24.575	98.30	75-125
	94	n-Propylbenzene	25.000	24.026	96.10	75-125
	95	2-Chlorotoluene	25.000	24.013	96.05	75-125
	97	1,3,5-Trimethylben	25.000	24.534	98.14	75-125
	96	4-Chlorotoluene	25.000	23.985	95.94	75-125
M	98	1,2-Dichloroethene	50.000	56.780	113.56	75-125
	99	tert-Butylbenzene	25.000	23.601	94.40	75-125
	101	1,2,4-Trimethylben	25.000	23.738	94.95	75-125
	102	sec-Butylbenzene	25.000	24.123	96.49	75-125
	103	1,3-Dichlorobenzen	25.000	23.511	94.05	75-125
	105	p-Isopropyltoluene	25.000	23.245	92.98	75-125
	106	1,4-Dichlorobenzen	25.000	24.534	98.14	75-125
	108	n-Butylbenzene	25.000	24.262	97.05	75-125
	107	1,2-Dichlorobenzen	25.000	25.383	101.53	75-125
	109	1,2-Dibromo-3-Chlo	25.000	27.930	111.72	75-125
	110	1,3,5-Trichloroben	25.000	25.759	103.04	75-125
	111	1,2,4-Trichloroben	25.000	24.389	97.56	75-125
	112	Hexachlorobutadien	25.000	24.093	96.37	75-125
	113	Naphthalene	25.000	24.916	99.66	75-125
	114	1,2,3-Trichloroben	25.000	24.742	98.97	75-125
M	93	Xylene (total)	75.000	72.850	97.13	75-125

RECOVERY REPORT

Client Name: Client SDG: 090705
Sample Matrix: LIQUID Fraction: VOA
Lab Smp Id: ICAL SPIKE
Level: LOW Operator: JDN
Data Type: MS DATA SampleType: BS
SpikeList File: ICALSPK.spk Quant Type: ISTD
Sublist File: all.sub
Method File: /var/chem/gcl16.i/090705.b/water16.m
Misc Info: ICAL SPIKE,1,9,WATER16.m,090705.b

SURROGATE COMPOUND	CONC ADDED ug/L	CONC RECOVERED ug/L	% RECOVERED	LIMITS
$ 39 Dibromofluorometha	25.000	26.024	104.10	77-118
$ 46 1,2-Dichloroethane	25.000	25.559	102.24	62-127
$ 66 Toluene-d8	25.000	25.464	101.86	81-126
$ 88 p-Bromofluorobenze	25.000	25.629	102.52	67-132

CONTINUING CALIBRATION COMPOUNDS

Instrument ID: gcl16.i Injection Date: 08-SEP-2005 08:15
Lab File ID: 16c0908.d Init. Cal. Date(s): 07-SEP-2005 07-SEP-2005
Analysis Type: WATER Init. Cal. Times: 10:57 18:08
Lab Sample ID: VSTD025 Quant Type: ISTD
Method: /var/chem/gcl16.i/090805.b/water16.m

	COMPOUND	RRF / AMOUNT	RF25	CCAL RRF25	MIN RRF	%D / %DRIFT	MAX %D / %DRIFT	CURVE TYPE
	1 Dichlorodifluoromethane	26.36728	25.00000	0.65311	0.010	5.46911	50.00000	Linear
	2 Chloromethane	0.80912	0.88785	0.88785	0.100	9.72950	50.00000	Averaged
	3 Vinyl chloride	0.57081	0.61073	0.61073	0.010	6.99295	20.00000	Averaged
	5 Bromomethane	25.09460	25.00000	0.10188	0.010	0.37838	50.00000	Linear
	7 Chloroethane	28.29277	25.00000	0.21752	0.010	13.17109	50.00000	Quadratic
	8 Trichlorofluoromethane	0.61016	0.67432	0.67432	0.010	10.51672	50.00000	Averaged
	10 Acrolein	0.01133	0.00961	0.00961	0.001	-15.15250	50.00000	Averaged
	12 Trichlorotrifluoroethane	0.35811	0.35108	0.35108	0.010	-1.96278	50.00000	Averaged
	11 1,1-Dichloroethene	0.30504	0.30256	0.30256	0.010	-0.81367	20.00000	Averaged
	13 Acetone	24.59375	25.00000	0.09206	0.010	-1.62500	50.00000	Linear
	15 Carbon Disulfide	1.09706	1.14460	1.14460	0.010	4.33309	50.00000	Averaged
	16 Acetonitrile	184	200	0.02486	0.001	-7.76741	50.00000	Linear
	19 Methylene chloride	0.57076	0.50822	0.50822	0.010	-10.95640	50.00000	Averaged
	20 Acrylonitrile	0.11211	0.09493	0.09493	0.001	-15.32595	50.00000	Averaged
	22 Methyl-tert-Butyl Ether	1.14710	1.06188	1.06188	0.010	-7.42929	50.00000	Averaged
	21 trans-1,2-Dichloroethene	0.59113	0.54887	0.54887	0.010	-7.14884	50.00000	Averaged
	26 1,1-Dichloroethane	1.19731	1.12977	1.12977	0.100	-5.64140	50.00000	Averaged
	27 Vinyl Acetate	24.73925	25.00000	0.78791	0.010	-1.04300	50.00000	Linear
	31 cis-1,2-Dichloroethene	0.60774	0.57665	0.57665	0.010	-5.11569	50.00000	Averaged
	30 2,2-Dichloropropane	0.80711	0.81703	0.81703	0.010	1.22844	50.00000	Averaged
	32 2-Butanone	0.19488	0.18081	0.18081	0.010	-7.22038	50.00000	Averaged
	33 Propionitrile	0.02663	0.02332	0.02332	0.001	-12.43315	50.00000	Averaged
	35 Bromochloromethane	0.24243	0.22634	0.22634	0.010	-6.63941	50.00000	Averaged
	37 Tetrahydrofuran	0.10084	0.09299	0.09299	0.010	-7.78679	50.00000	Averaged
	38 Chloroform	0.99184	0.93054	0.93054	0.010	-6.17951	20.00000	Averaged
$	39 Dibromofluoromethane	0.46053	0.48751	0.48751	0.010	5.85946	50.00000	Averaged
	40 1,1,1-Trichloroethane	0.81988	0.79013	0.79013	0.010	-3.62811	50.00000	Averaged
	45 1,1-Dichloropropene	0.82313	0.80043	0.80043	0.010	-2.75779	50.00000	Averaged
	44 Carbon tetrachloride	0.37428	0.38830	0.38830	0.010	3.74403	50.00000	Averaged
$	46 1,2-Dichloroethane-d4	0.30367	0.32675	0.32675	0.010	7.60159	50.00000	Averaged
	48 Benzene	1.52647	1.43805	1.43805	0.010	-5.79258	50.00000	Averaged
	49 1,2-Dichloroethane	0.42645	0.40390	0.40390	0.010	-5.28939	50.00000	Averaged
	55 Trichloroethene	0.36376	0.34478	0.34478	0.010	-5.21833	50.00000	Averaged
	57 1,2-Dichloropropane	0.38961	0.37964	0.37964	0.010	-2.55885	20.00000	Averaged
	58 Dibromomethane	0.14531	0.14414	0.14414	0.010	-0.80228	50.00000	Averaged
	60 Bromodichloromethane	0.33533	0.34172	0.34172	0.010	1.90567	50.00000	Averaged

CONTINUING CALIBRATION COMPOUNDS

Instrument ID: gcl16.i Injection Date: 08-SEP-2005 08:15
Lab File ID: 16c0908.d Init. Cal. Date(s): 07-SEP-2005 07-SEP-2005
Analysis Type: WATER Init. Cal. Times: 10:57 18:08
Lab Sample ID: VSTD025 Quant Type: ISTD
Method: /var/chem/gcl16.i/090805.b/water16.m

	COMPOUND	RRF / AMOUNT	RF25	CCAL RRF25	MIN RRF	%D / %DRIFT	MAX %D / %DRIFT	CURVE TYPE
	63 2-Chloroethylvinylether	21.25642	25.00000	0.01657	0.010	-14.97433	50.00000	Quadratic
	64 cis-1,3-Dichloropropene	0.46277	0.46750	0.46750	0.010	1.02266	50.00000	Averaged
	65 4-Methyl-2-pentanone	0.20641	0.20217	0.20217	0.010	-2.05224	50.00000	Averaged
$	66 Toluene-d8	1.13570	1.25208	1.25208	0.010	10.24708	50.00000	Averaged
	67 Toluene	0.97745	0.91395	0.91395	0.010	-6.49672	20.00000	Averaged
	68 trans-1,3-Dichloropropene	0.36120	0.36743	0.36743	0.010	1.72410	50.00000	Averaged
	70 1,1,2-Trichloroethane	0.36516	0.33649	0.33649	0.010	-7.85168	50.00000	Averaged
	71 Tetrachloroethene	26.37725	25.00000	0.44351	0.010	5.50901	50.00000	Linear
	72 1,3-Dichloropropane	0.48421	0.47978	0.47978	0.010	-0.91429	50.00000	Averaged
	73 2-Hexanone	25.38083	25.00000	0.14503	0.010	1.52334	50.00000	Quadratic
	74 Dibromochloromethane	24.75698	25.00000	0.23988	0.010	-0.97206	50.00000	Linear
	75 1,2-Dibromoethane	0.20546	0.19508	0.19508	0.010	-5.05163	50.00000	Averaged
	78 1-Chlorohexane	0.81425	0.83051	0.83051	0.010	1.99758	50.00000	Averaged
	77 Chlorobenzene	26.80380	25.00000	1.14801	0.300	-7.21520	50.00000	Linear
	79 1,1,1,2-Tetrachloroethane	0.32141	0.33312	0.33312	0.010	3.64481	50.00000	Averaged
M	98 1,2-Dichloroethene (total)	0.59944	0.56276	0.56276	0.010	-6.11818	50.00000	Averaged
	80 Ethylbenzene	0.68689	0.68418	0.68418	0.010	-0.39519	20.00000	Averaged
	81 p,m-Xylene	1.60399	1.61372	1.61372	0.010	0.60652	50.00000	Averaged
M	93 Xylene (total)	1.57685	1.57600	1.57600	0.010	-0.05402	50.00000	Averaged
	82 o-Xylene	1.57685	1.57600	1.57600	0.010	-0.05402	50.00000	Averaged
	83 Styrene	1.17601	1.27711	1.27711	0.010	8.59655	50.00000	Averaged
	84 Bromoform	26.79109	25.00000	0.12566	0.100	7.16438	50.00000	Quadratic
	85 Isopropylbenzene	3.93312	4.02590	4.02590	0.010	2.35898	50.00000	Averaged
$	88 p-Bromofluorobenzene	0.49755	0.55569	0.55569	0.010	11.68508	50.00000	Averaged
	90 1,1,2,2-Tetrachloroethane	0.57627	0.54268	0.54268	0.300	-5.82860	50.00000	Averaged
	89 Bromobenzene	0.88241	0.86080	0.86080	0.010	-2.44879	50.00000	Averaged
	91 1,2,3-Trichloropropane	0.17144	0.16451	0.16451	0.010	-4.03951	50.00000	Averaged
	94 n-Propylbenzene	4.73175	4.84208	4.84208	0.010	2.33161	50.00000	Averaged
	95 2-Chlorotoluene	2.86291	2.74675	2.74675	0.010	-4.05772	50.00000	Averaged
	97 1,3,5-Trimethylbenzene	3.30325	3.36079	3.36079	0.010	1.74183	50.00000	Averaged
	96 4-Chlorotoluene	3.17431	3.21254	3.21254	0.010	1.20433	50.00000	Averaged
	99 tert-Butylbenzene	2.92293	2.84457	2.84457	0.010	-2.68097	50.00000	Averaged
	101 1,2,4-Trimethylbenzene	3.44564	3.43948	3.43948	0.010	-0.17894	50.00000	Averaged
	102 sec-Butylbenzene	4.44360	4.49711	4.49711	0.010	1.20439	50.00000	Averaged
	103 1,3-Dichlorobenzene	1.84644	1.80378	1.80378	0.010	-2.31023	50.00000	Averaged

CONTINUING CALIBRATION COMPOUNDS

Instrument ID: gcl16.i Injection Date: 08-SEP-2005 08:15
Lab File ID: 16c0908.d Init. Cal. Date(s): 07-SEP-2005 07-SEP-2005
Analysis Type: WATER Init. Cal. Times: 10:57 18:08
Lab Sample ID: VSTD025 Quant Type: ISTD
Method: /var/chem/gcl16.i/090805.b/water16.m

COMPOUND	RRF / AMOUNT	RF25	CCAL RRF25	MIN RRF	%D / %DRIFT	MAX %D / %DRIFT	CURVE TYPE
105 p-Isopropyltoluene	3.60102	3.68538	3.68538	0.010	2.34278	50.00000	Averaged
106 1,4-Dichlorobenzene	25.10816	25.00000	1.80534	0.010	0.43264	50.00000	Linear
108 n-Butylbenzene	3.33787	3.45443	3.45443	0.010	3.49216	50.00000	Averaged
107 1,2-Dichlorobenzene	25.38389	25.00000	1.53908	0.010	1.53556	50.00000	Linear
109 1,2-Dibromo-3-Chloropropane	26.01837	25.00000	0.07653	0.010	4.07349	50.00000	Quadratic
111 1,2,4-Trichlorobenzene	1.07609	1.04187	1.04187	0.010	-3.18016	50.00000	Averaged
112 Hexachlorobutadiene	0.65488	0.63541	0.63541	0.010	-2.97357	50.00000	Averaged
113 Naphthalene	23.31067	25.00000	1.69668	0.010	-6.75734	50.00000	Linear
114 1,2,3-Trichlorobenzene	24.20102	25.00000	0.90610	0.010	-3.19590	50.00000	Linear

Average %D / Drift Results.

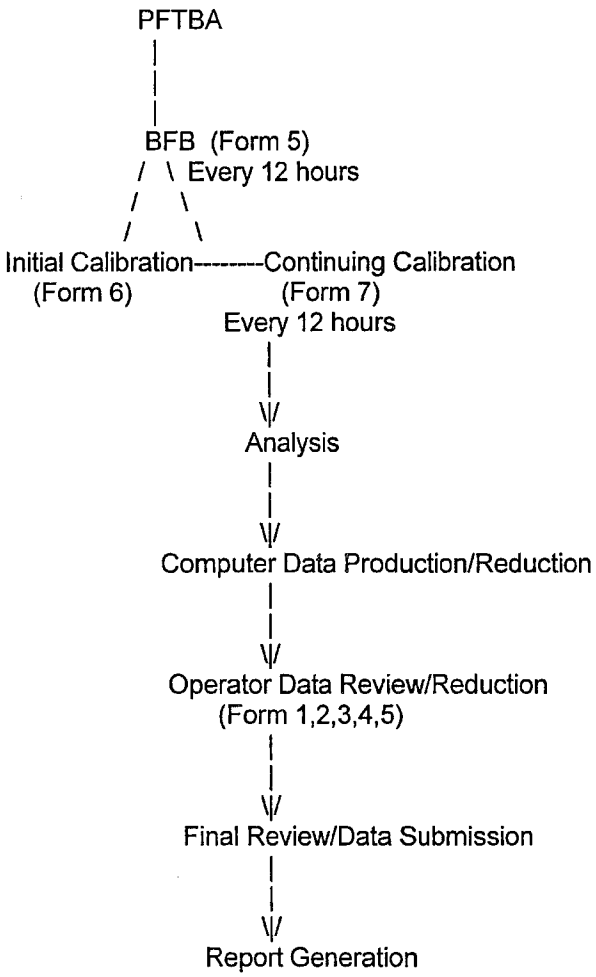
Calculated Average %D/Drift = 4.76823
Maximun Average %D/Drift = 15.00000
* Passed Average %D/Drift Test.

Attachment 5.

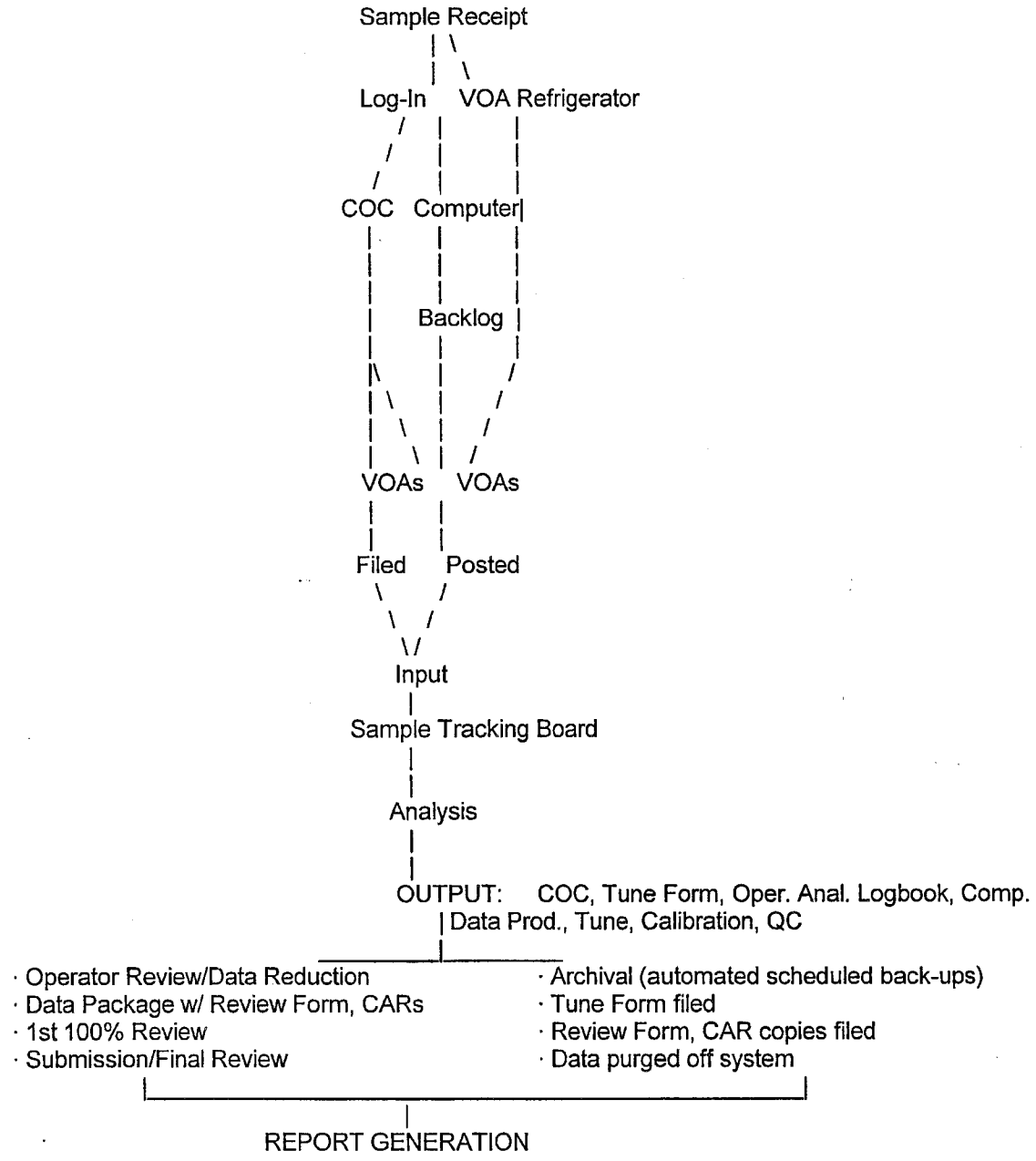
Example: Analysis and Sample Tracking Flowcharts

ANALYSIS SCHEME FLOWCHART

(Terms defined in the Section 9)



Sample Tracking Flowchart (for EACH unique Job)



Attachment 6.

Example: Data Review Form

STL Chicago

GCMS DATA REVIEW CHECKLIST

Site Name:_____ Primary Reviewer:_____ Review Date:_____

JOB Number: _____ Secondary Reviewer:_____ Review Date:_____

No. of Samples/Matrix: a) _____ WATER b) _____ SOIL c) _____ SPLP / TCLP d) _____ Other (_____)

Method: a) VOA _____ 5030_____ Encores: 5035–High _____ 5035-Low_____ b) BNA _____

Report Type: a) MDL U b) RL U c) ND d) Breach e) P1 / P2 (Printed QC must match PM selected Report Type)

TASK	PRI REV	SEC REV	COMMENTS
LAB CHRON: 1) Matches Big Board (Job Analysis History)			
2) Matches Raw Data (Form 4 / 5)			
3) Note Sample dilutions and list reason. a) High Sample Conc. b) Interference present IF **original** and **re-run** are to be reported in LabNet Re-log Samples (Indicate data type used) Re-Analyzed (RE) Re-Extracted (RA) Dilution (DL)			Smp # Original Dilution Comments BNA Only: Final Volume Adjustment _____
4) Sample Hold Times Met			
5) Proper Prep Links Created S-F6: Routine Preps; 5035PL; 5035PH S-F9: TCLP; SPLP ; 5035 Archon Purge & Trap			
Incomplete JOB Status Report reveals No Outstanding Data			
PROJ. REQ. MET: 1) Sample Detection Limit Met			
2) Reported J values meet reporting criteria			
3) Method Blank Detection Limits Met			
4) Project Specific Compounds of Concern : Yes No			
LabNet Report matches Quant Report: Sample weights / Volumes / % Moisture / Factors verified			
Manual Integration documentation / verification complete			
FORM 2: Surrogate Recoveries Within Limits Statistical Limits _____ Method Limits _____ Project Limits _____(S-F10 used to Clone By Project) AFCEE___; LCG___; QAPP___ Directed Note to PM: Yes / No			Smp # Original Re-analysis Comments
FORM 3: MS/MSD Recoveries Acceptable Statistical Limits _____ Method Limits _____ Project Limits _____(S-F10 used to Clone By Project) AFCEE___; LCG___; QAPP___ Directed Note to PM: Yes / No			Smp # _____ MS MSD RPD
FORM 3: LCS Recoveries Acceptable (LCD if no MS/MSD) Statistical Limits _____ Method Limits _____ Project Limits _____(S-F10 used to Clone By Project) AFCEE___; LCG___; QAPP___ Directed Note to PM: Yes / No			Batch # _____ Batch # _____ Batch # _____ Batch # _____ Batch # _____ Batch # _____

TASK	PRI REV	SEC REV	COMMENTS
FORM 5: Tuning Criteria Met			
FORM 6: Initial Calibration Criteria Met			
ICAL Spike Required: Yes No Control Limit applied: _____			
FORM 7: Daily Calibration (CCV) Criteria Met			
MRL Check Required: Yes No (LCG Requirement – Before and after Sample analysis) Control Limit Applied: _____			Before: After: Batch # _____ Batch # _____ Batch # _____ Batch # _____ Batch # _____
FORM 8: Internal Standards Criteria Met Directed Note to PM: Yes / No			Smp # Original Re-analysis Comments
LabNet Batch Status Report Displays Data at RPT / RVWD Status	RPT	RVWD	
RAW DATA: 1) Raw Data Verified/Complete			
2) Raw Data Matches Forms			
3) 5035 Prep Log page present / verified			
4) Quant Report Matches Spectra			
5) Manual integration reports (befores and afters) present (when required by client) and reason correctly documented and approved. Manual Integration Summary Printed: Yes No			File ID:
NARRATIVE: 1) Holding Times			
2) Method References			
3) % Recoveries / RPD's			
4) Analytical Difficulties/Typos/CAR's Directed Note to PM: Yes / No			
Manual Calculation of On Column result: Response Factor (Smp) x Concentration of IS IS Response Factor (Smp) Cmpd. RRF (Cont.Calib)			Sample : _____ Compound: _____

Additional Comments:

Attachment 7.

P-T-001: STL Corporate Policy for the Selection of Calibration Points

Approvals and Signatures

Senior Vice President & Chief Operating Officer:	Dr. Keith C. Wheatstone	Date: 10/6/2004
Vice President, Client and Operations Services:	Dr. Charles W. Carter	Date: 10/6/2004
Technology Director:	Dr. Richard Burrows	Date: 9/8/2004

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1.0 PURPOSE

This policy describes Severn Trent Laboratories (STL) requirements for determination of the number of points, and removal of points from calibration curves.

2.0 SCOPE

Applies to all multi-level initial calibrations.

3.0 POLICY

3.1 If the number of data points required for an initial calibration is defined in the method, Quality Assurance (QA) plan, published report, or previously approved Standard Operating Procedure (SOP) that is what will be used.

3.2 In the cases not defined in Section 1, the number of data points will be determined by the technical director based on the Data Quality Objectives (DQOs) for precision and accuracy to be met by the method.

Examples:

A. Need to analyze a new pesticide in water and a published method does not exist. The data will be used to screen samples by UV-HPLC at a waste site for further remediation, using DQOs that require precision/accuracy of ± 50%.

The Technical director selects 2 data points to represent the range of the expected concentration of pesticide and based on 4 Laboratory Control Samples (LCS), the recoveries ranged from 78-104%. Therefore, 2 data points are sufficient for initial calibration for this method.

NOTE: Calibration curves with less than 3 points should only be used after discussion with the client that the data quality objectives will be met.

B. Same compound as above but being measured in laboratory for meeting regulatory limit of 0.05 mg/L in water. Precision and accuracy of ± 20% required.

A five-point calibration is used, based on similar requirements in published methods with similar objectives and the high level of precision and accuracy required.

As noted above for methods where technical director selects the number of data points to meet DQOs for precision and accuracy, the 4 LCS used in the demonstration of capability will be used to assure those DQOs are met. The SOP will then be approved by the Quality Assurance (QA) Manager.

3.3 Removal of Points from a Calibration Curve

3.3.1 Removal or replacement of levels from the middle of a calibration (i.e., levels other than the highest or lowest) is not permitted unless an injection or instrument problem confined to that point can be clearly documented as described below. Removal of points for individual analytes from levels other than the highest and lowest is not permitted in any event.

3.3.2 If the analyst can document that a level is not valid because of an injection or instrument problem confined to that run, the level may be excluded if the curve still has sufficient levels, or the run may be repeated once only. The whole level (all compounds) must be

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removed or replaced. The curve is evaluated with the level removed or replaced. If the curve still fails to meet criteria, then corrective action must be taken and the whole curve reanalyzed. Corrective action may include, but is not limited to, instrument maintenance and/or re-preparation of standards.

3.3.3 One of the following conditions must be satisfied to allow removal or replacement of a level:

- The data file is corrupted and unusable or the run is interrupted before completion.
- The analyst observes and documents a problem such as leaking of a purge vessel.
- For internal standard methods, the recovery of the internal standards is less than 70% or greater than 130% of the recovery in the other standards, or the amount of analyte recovered is less than 70% or greater than 130% of the expected values (indicating an improperly made up standard).
- For external standard methods, the unit response of the analyte is less than 70% or greater than 130% of the average unit response for the analyte in the other calibration standards (indicating an improperly prepared standard or bad injection).

3.3.4 When using autosamplers with discrete sample pathways for different samples (such as 16 port purge and trap autosamplers) the level to be replaced must be reanalyzed on the same port or that port must be excluded from sample analysis until corrective action is performed and verified by successful analysis of a continuing calibration standard on that port.

3.3.5 The reason for replacing the level **must** be documented in the run log. The fact that the curve passes criteria with the level removed is **not** alone sufficient evidence to document an injection or instrument problem confined to the level.

3.3.6 Removal of the highest or lowest levels is permitted, but the calibration range must be adjusted accordingly. If the lowest level is removed then the reporting limit is raised to be equivalent to the lowest level used in the calibration curve. In any event the number of levels remaining in the calibration must be at least that required by the method.

3.3.7 Removal of the highest or lowest point is permitted on a compound specific basis. This may be necessary when strongly responding and poorly responding analytes are included in the same standard mix at the same level. Each compound must have at least the minimum number of calibration levels required by the method.

4.0 RESPONSIBILITIES

All STL associates utilizing methods involving multi-point calibrations are required to follow this policy.

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5.0 ATTACHMENTS

Not Applicable.

6.0 REVISION HISTORY

Revision 3: Updated by Richard Burrows, Technology Director; 9/8/2004.
Section 3.2: Amended 'NOTE'.
Section 3.3.3, bullet #4, text reworded for clarification.

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Attachment 8.

S-Q-004: STL Corporate SOP for Manual Integrations

Approvals and Signatures

Senior Vice President & Chief Operating Officer:	Dr. Keith C. Wheatstone	Date: 9/20/2004
Vice President, Client and Operations Services:	Dr. Charles W. Carter	Date: 9/20/2004
Corporate Quality Director:	Raymond J. Frederici	Date: 9/20/2004

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1.0 PURPOSE

This document describes STL's policy for proper manual peak integrations and requirements for documentation and review of manual peak integrations performed during the course of analyses.

2.0 SCOPE

This policy shall be enforced and followed throughout the laboratory. It applies to all STL laboratories for any analytical procedure involving identification or quantitation based on peak

analysis (e.g., GC, GC/MS, HPLC, IC). Each laboratory may have supplemental manual integration procedures or an addendum to this policy that describes additional details necessary to implement and enforce this policy. Any supplemental procedure or addendum must adhere to the requirements set forth in this policy.

3.0 POLICY

3.1 Supervisors must ensure proper training to all analysts and data reviewers using peak integration techniques. Analysts and data reviewers using peak integration techniques must be familiar with this policy and the applicable data processing system. This is to ensure that integration parameters are used in a manner that minimizes the need for manual integrations and that circumstances requiring manual integrations are performed in accordance with acceptable practices, documented and reviewed by a peer or supervisor. Audit trails or tracking systems MUST BE activated when the chromatographic system has this feature.

3.2 In some situations, manual integrations are necessary to compensate for imperfect chromatography, but manual integration must be performed ONLY when necessary. Baseline upsets, coelution and peak shape variation can sometimes complicate automatic integration and analyst intervention through manual integration may be required to assure consistency between area assignment for standards and samples.

3.3 Proper consistent manual integration is a critical quality control requirement. Appropriate manual integration is integration that can be technically justified. Manual integrations shall not be used to manipulate analytical results in order to meet method- or project-specific quality control (QC) acceptance criteria. Integration below the baseline is never appropriate. Inappropriate and inconsistent chromatographic peak integration to meet quality requirements is never allowed, nor is it to be used as a substitute for corrective action on the chromatographic system. Willful failure to follow this policy shall result in disciplinary action, up to and including termination.

3.4 The same integration technique must be applied **consistently** to any chromatogram i.e., field samples, calibration standards, calibration verification standards, and other applicable QC, etc., within the same analytical batch affected by the manual integration. Consistency in integration between standards and samples is one of the most important considerations in quantitative chromatographic analysis. Examples of appropriate and improper integration can be found in Appendix I and II.

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4.0 REASONS TO MANUALLY INTEGRATE

4.1 Undetected Peak

Routine mass spectrometer instrument tuning or the analysis of highly contaminated samples sometimes causes the relative abundances of ions of compounds present to deviate from reference criteria causing a peak to go undetected by the data system. A slight shift in chromatographic retention times can result in undetected peaks or false positive identification of compounds. If sample surrogate(s) retention times (RTs) shift, sample peaks need to be reviewed to ensure proper peak identification.

4.2 Incorrect Peak Integration

- Peak has small amount of splitting and the whole peak area was not integrated.
- Peaks close in retention times utilizing the same quantitation ions often integrate together as one peak, for example: ethylbenzene, xylenes; dichlorobenzenes, benzo(b)fluoranthene and benzo(k)fluoranthene.

4.3 Baseline Correction

- Matrix interferences caused by contaminated samples may interfere with calibrated compounds.

4.4 Other Examples of Events Requiring Manual Integration

- Incorrectly identified peak, where the wrong peak is chosen by the data system. This can occur both with the primary and the secondary ions.
- To remove a shoulder from a peak or to integrate a peak that only appears as a shoulder.

5.1 DATA SYSTEM PROCEDURES

5.1 The chromatography system's method integration parameters must be optimized to the greatest extent possible so compounds are properly identified and integrated with minimal operator intervention. (Note: even when integration parameters work properly for calibration standards, the analyst must ensure the integration is appropriate on all samples. The analyst must not assume that the chromatography system will automatically apply the correct integration). When manual integrations are necessary to identify peaks as targets (determine the RT), the calibration standards must be reprocessed after updating the retention times to demonstrate that the data system integration parameters are set properly. The following steps are required:

5.1.1 Process the file using the current data system parameters for the mid-level standard.

5.1.2 Identify all of the target compounds and assign the correct RT to each target. Manual integrations at this point do not have to be documented and must not be included in the calibration evaluation.

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5.1.3 Reprocess the data and confirm that all of the targets can be identified and properly integrated. If the targets cannot be identified and properly integrated, adjust the integration parameters and reprocess the data. This is an important step. If the data system cannot reliably detect and integrate the targets in the mid-level standard, the probability of properly identifying and quantifying the targets in the remaining standards and samples are low.

5.1.4 Process the remaining calibration standards and confirm that the data system can routinely and properly identify the target compounds at each calibration level. Pay particular attention to the lowest level standard because this standard typically defines the reporting limit (RL). The integration parameters should allow for detection of the target compounds down to the quantitation limit or reporting limit.

5.1.5 The integration parameters set at the initial calibration must remain in use until the next calibration is performed, except as noted in 4.3. Manual integrations are used only when the conditions listed in Section 3.0 are encountered. Manual integration is not to be used solely to meet QC criteria, nor is it to be used as a substitute for corrective action on the chromatographic system.

5.1.6 Any manual integration of a chromatographic peak or group of peaks must be documented. In all instances where the data system report has been edited or where manual integration has been performed, the chromatographic system operator must clearly identify such edits or manual procedures as listed below:

- Manual integrations indicated on expanded scale "after" chromatograms.
- Re-integration technique marked, if available, on the data system
- Technical justification for manual integration.
- Analyst's initials and date. (data system application of analyst name or initials is acceptable so long as the data system allows the analyst to log in as himself or herself and has password control)

5.1.7 Project specific, client, program or STL laboratory specific requirements for manual integration may exceed the requirements of this policy. In those instances, the more specific requirements will apply or written approval allowing a deviation from the requirement must be received. For example:

- Requiring the before and after printing of the chromatograms
- Handwritten or electronic initialing and dating the changes made to the report
- Hardcopy printout of the EICP of the quantitation ion displaying the manual integration included in the raw data for all standards and samples, this applies to internal standards and surrogates as well.
- Requiring manual integrations to be documented in the project or case narrative

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5.2 Data reviewers shall confirm that documentation of manual integration is complete and that each manual integration is appropriate. This inspection shall be documented. At a minimum, the information required in Section 5.1.6 must be reviewed.

5.3 If integration indicates problems with analytical instrumentation, investigate the problem and take action to correct it. If poor chromatography routinely interferes with the ability to identify and quantify components; is a result of delayed system maintenance; and is not inherent in the system, such as (benzoic acid for Method 8270; benzo(b)anthracene and benzo(k)anthracene merging with column age; and dichlorobutenes merging with column age), then instrument maintenance must be performed. If instrument and data conditions have changed such that the default integration parameters no longer work as effectively, it is acceptable to change the default parameters and reprocess all affected data, including the associated standards, lab QC, and field samples, using the new integration parameters. Further manual manipulations after this reprocessing must be treated as manual integrations. The reason for reprocessing must be documented and approved.

5.4 Manual integrations on some data systems (e.g., Multichrom) may consist of adjusting integration parameters on a by-sample basis. Changes such as these must be documented.

5.5 Any deficiencies must be resolved with the analyst or their supervisor before the results are approved and released from the analytical department. Any questions arising from review of the documentation must be investigated in the electronic record, when available, prior to data acceptance. Any failures to complete these requirements shall be described in a non-conformance report.

5.6 Any concerns about violations of this policy must be reported to the facility Quality Manager, Laboratory Director or the Corporate Quality Director.

5.7 Electronic data surveillance is performed using *Mint Miner*™ Software. This software allows the user to connect to a workstation or archived data source and evaluate the audit trails in the electronic data file (refer to WI-STL-002/A-08/03).

6.0 DEFINITIONS

- Integration: The determination of the area or height under a curve (peak).

- Manual integrations: Include any adjustments to measurements of analytical peaks not applied equally to all applicable samples and QC parameters in an analytical batch by the data acquisition system. For the purpose of this policy, a manual integration has been performed if results for any of the analyses could not be duplicated by another analyst using the indicated calibration and standard peak integration protocol. Manual adjustments to peaks can include baseline changes, retention time window adjustments, changes to peak identification in samples (calibration standards' changes as required are exempt), manual peak height measurements, or changes to the formula used to

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model analytical peak areas or changes to background subtraction algorithms for GC/MS tuning. Although the latest analytical instruments are equipped to perform automatic integrations, manual integrations are sometimes necessary to accurately analyze samples if peaks are poorly resolved, exhibit tailing, the baseline drifts or is noisy, or other similar situations.

- Chromatograms: In the context of this policy, chromatograms are not necessarily limited to the output of chromatography instruments or automated data systems. They can include strip charts, integrator printouts, computer screen dumps, or any graphic display of a continuous signal from an analytical detector.

- Chromatography: A separation technique involving differential retention of components between stationary and mobile phases.

- Baseline: The chromatographic signal plotted as a function of time in the absence of signal construction from components of interest.

- Peak: An increase in signal from baseline to a maximum and then back to baseline.

- Coelution: the concurrent elution of two or more compounds to the detector at the same time.

- Elution: The process of movement of compounds from the chromatographic system.

- "Wavy" Baselines: A "wavy" baseline can be caused by minor impurities in carrier gas or solvent.

- Negative Spikes: Negative spikes in chromatograms are sudden upsets in chromatographic signal below the normal baseline.

- Sudden Rise in Baseline: A rise in the baseline is caused by several factors including high concentration of components in the sample and by normal column bleed.

- Carry-over: Carry over results from system contamination from previous analyses and results in signal unrelated to the current analysis.

- Peak Tailing: Peak tailing is a delayed return of a peak to chromatographic baseline and could be related to a delay of compound elution from the chromatographic system by adsorption or dead volume effects.

- Interference Peaks or Fused Peaks: Peaks that partially or totally coelute with the peak of interest.

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7.0 APPENDICES

- Appendix I. Examples of Peak shape and Proper integration Documenting Manual Integrations
- Appendix II. Examples of Improper Integration and Inflection Point Guidance

8.0 TRAINING MODULE

- Acceptable Manual Integration Practices, September 2004, Version 1.1: T-Q-004.

9.0 REVISION HISTORY

- Revision 1; dated 12/1/01
- Revision 2; Amended Section 5.7; dated 9/17/04.

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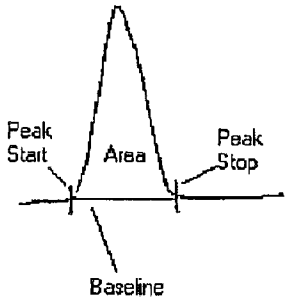
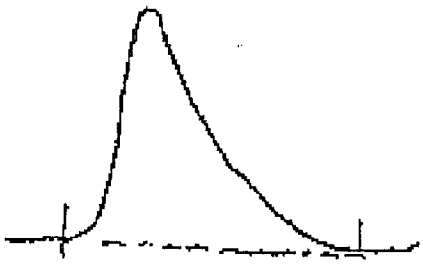
Appendix I.

Examples of Peak shape and Proper integration Documenting Manual Integrations

Ideal peak (Gaussian Shape) The start of integration is where the peak begins to rise from the background, and the end is where the peak returns to background.	
Tailing Peak Tailing peaks result from surface adsorption effects or dead volume in the instrument. When integrating tailing peaks, include only and all area that can be attributed to compound. If the baseline rises, the integration line should rise with the baseline.	

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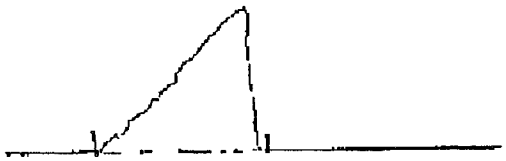
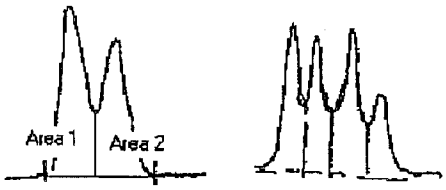
Fronting Peak Fronting peaks generally result from column overload and/or overcapacity. An example is benzoic acid on a 5% phenyl phase. In some cases, it is inherent in the analysis, in others, it is indicative of problems in the system. The analyst must have knowledge of their system. To integrate these peaks, it is important to have prior knowledge of how the compound acts when overloading versus co-eluting with a contaminate peak.	
Fused Peaks Fused peaks are near coeluters with some separation. They will occur in calibration mixes as well as real samples. To integrate, split the components with a vertical drop from the valley to the baseline.	
Hydrocarbon Envelope For semivolatile hydrocarbon analysis, most fuels produce "humpograms" like this one. Integration shall be performed in accordance with method, program or client specific requirements.	
Peak on a Baseline Rise Aside from hydrocarbon analysis, which uses the total area within a window for quantitation, baseline variations are not integrated. Therefore, skim the baseline rise to integrate the peak properly.	

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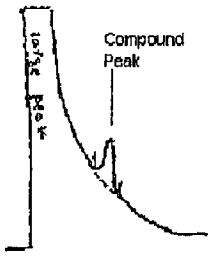
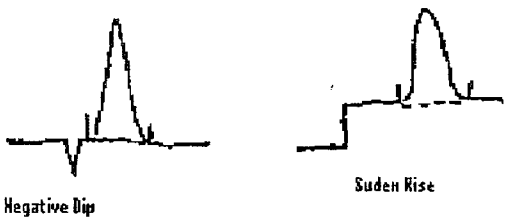
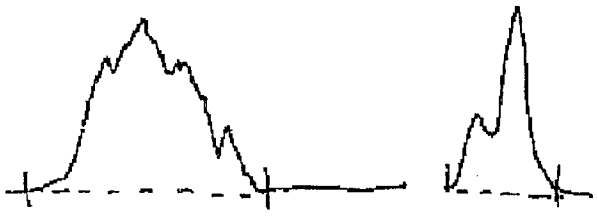
Skimmed Peak Use the tangent skimming functions of the integration software to correctly integrate small peaks on the tails of big peaks. Dropping vertical integration lines to the baseline of the big peak adds extra area which is not a part of the small peak, and results in high bias.	
Peak near a baseline upset Negative dips are common in ECD analysis, and the sudden rises in baseline are common with programmable fluorescence detectors where gain/wavelength switching occurs. Often, the default integration will go from the base of the negative peak to the far side of the peak of interest. This is results in high bias and is incorrect. Similarly, a default integration using the low part of the baseline rise and the far side of the peak of interest will also result in high bias and must be corrected.	
Split Peak Particularly in GC/MS analysis, low-level peaks may appear jagged or split. To integrate these properly, the analyst must have prior knowledge of the peak/compound chromatography.	

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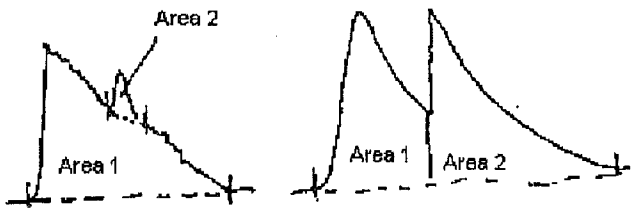
Fused tailing peaks These are very difficult to accurately quantify. It is best to do maintenance on the chromatography system to avoid this situation. To integrate these properly, the analyst should have prior knowledge of the compounds of interest. It is important to be consistent when integrating standards and samples.	

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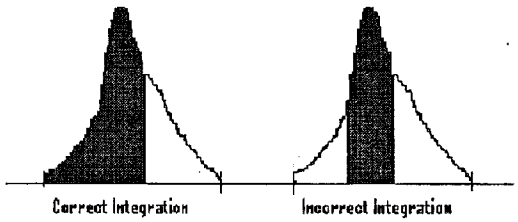
Appendix II.

Examples of Improper Integration and Inflection Point Guidance

An inflection point must be apparent when and if an integration point is drawn. For example:



When MS data has an inflection point in a peak, as shown in the example above, checking the underlying spectrum may be necessary to correctly manually integrate. On some chromatographic columns, for example, allyl chloride and carbon disulfide elute very close to each other, and they both share the primary characteristic ion mass 76. For both compounds mass 76 is the quantification mass. If two compounds can not be separated and a fused peak is going to be split at the inflection point, this can be correctly verified by looking at the spectra for each scan. In this example, the 76 peak may be fused, but the secondary ions will indicate which compound is present (carbon disulfide with secondary ion 78 and allyl chloride with secondary ions 41, 39 and 78).

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Severn Trent Laboratories Chicago
GC/MS Case Narrative

[redacted]

Job Number: 238907
VOA DATA:

1. All sample analyses were performed within the required hold time from the date of collection.

2. All of the Method Blanks and Extraction Blanks had target compounds below the reporting limits.

3. LCS 156607 had Trichloroflouromethane (140%) above the QAPP specified QC recovery limits (49-139). All other LCS (Laboratory Control Sample) samples had all controlled spike recoveries within the QAPP specified QC limits. All spike recoveries within the QAPP specified QC limits in the ICV.

4. Matrix Spike/Matrix Spike Duplicate analyses were not performed on this sample set.

5. All of the volatile samples had surrogate recoveries within the QAPP specified QC limits.

6. The soil samples were prepared using the low level Method 5035. All of the samples were analyzed following SW846 Method 8260B and 8000B. Trichlororfluoromethane (42%) and Acetone (50%) were above the 20% QAPP specified QC limits in the calibration verification for 9C0804A. Dichloroflouromethane (49%), Trichlororfluoromethane (63%), 1,1,1-Trichloroethane (20.8%), Dibromochloromethane (26%), Carbon Tetrachloride (44%), 1,2-Dichloroethane (37%), Tetrachloroethene (20.3%), 1,1,1,2-Tetrachlorocthene (25%), Bromoform (32%), 1,2-Dibromo-3-Chhloropropane (25%) and Hexachlorobutadiene (37%) were above the 20% QAPP specified QC limits in the calibration verification for 9C0804D . All of the other calibration criteria are met per method or QAPP (for minimum R-values for certain compounds). The low point in the initial calibration verifies the base reporting limits. The target compounds were quantitated using the initial calibration.

7. Samples 3 and 4 (vials A &B) had no internal standards injected by the analytical system in the 5035 prepared vials. The samples were reanalyzed after maintenance was performed on the instrument, using method 5030/8260 and reanalyzed. Sample 3 had two internal standards just below the acceptance limits as compared to the corresponding midpoint of the initial calibration. All other samples had internal standard areas and retention times within the SOP acceptance limits as compared to the corresponding midpoint of the initial calibration.

8. The soil samples were analyzed using the low-level soil method. The soil results and reporting limits were adjusted to account for the sample weights, the analytical procedure and on a dry weight basis.

=> 9. All manual integrations were performed following the laboratory's Manual Integration Standard Operating Procedure (SOP). The reason for manual integrations were documented and reviewed. A manual integration report has been provided.

Matthew A. Kobus
GC/MS Dept

8/24/15
Date

MANUAL INTEGRATION SUMMARY REPORT

Sample Name	Data File	Client ID	Compound
VSTD050	080405.b/9c0804a.d		Bromomethane
VSTD050	080405.b/9c0804a.d		4-Methyl-2-pentanone
LCS	080405.b/9s0804.d		Bromomethane
LCS	080405.b/9s0804.d		2-Butanone
LCS	080405.b/9s0804.d		4-Methyl-2-pentanone
LCD	080405.b/9t0804.d		Bromomethane
LCD	080405.b/9t0804.d		Trichlorofluoromethane
LCD	080405.b/9t0804.d		4-Methyl-2-pentanone

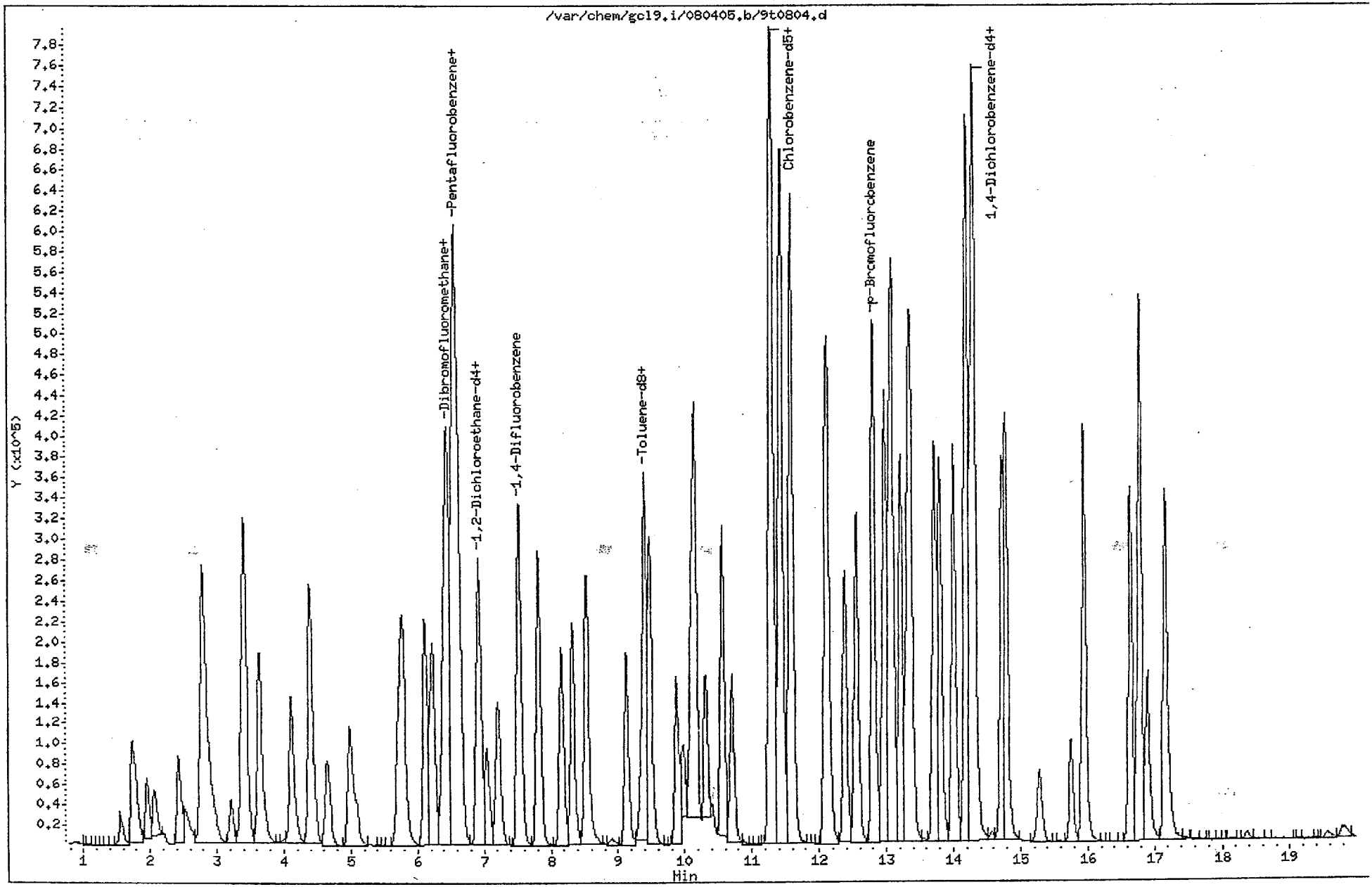
GP 8/23/5

Data File: /var/chem/gcl9.i/080405.b/9t0804.d
Date : 04-AUG-2005 19:42
Client ID: LCD156604
Sample Info: LCD

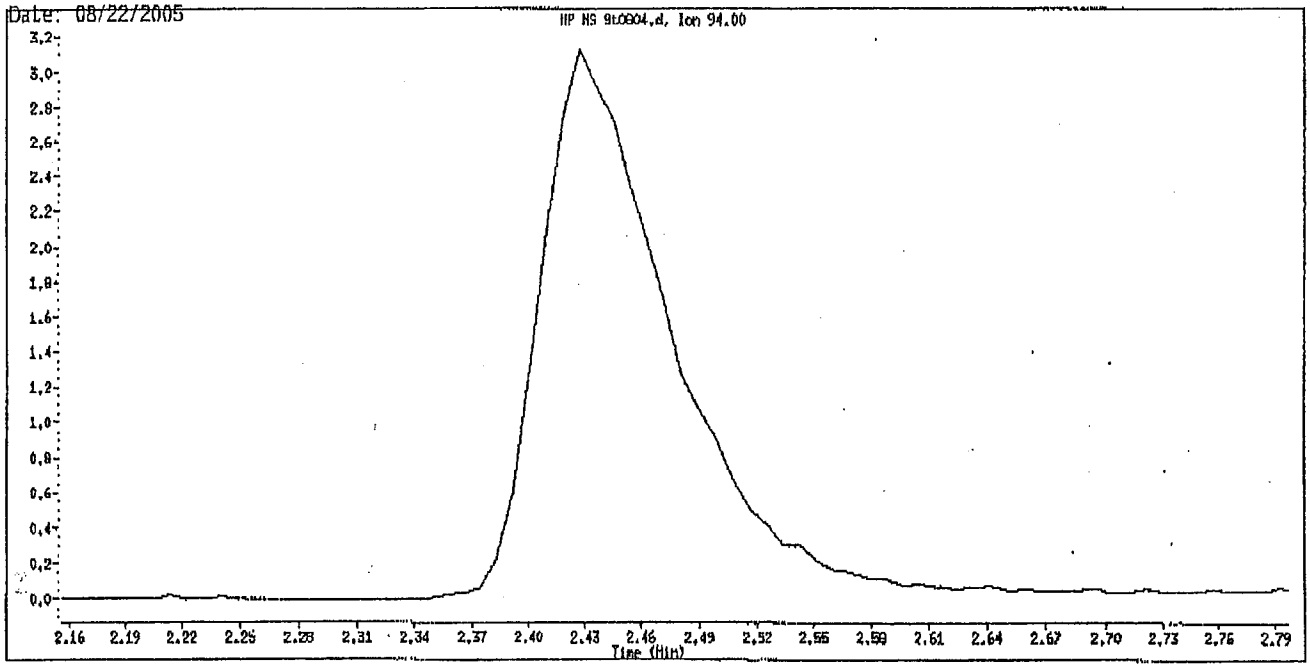
Instrument: gcl9.i

Operator: GES
Column diameter: 0.53

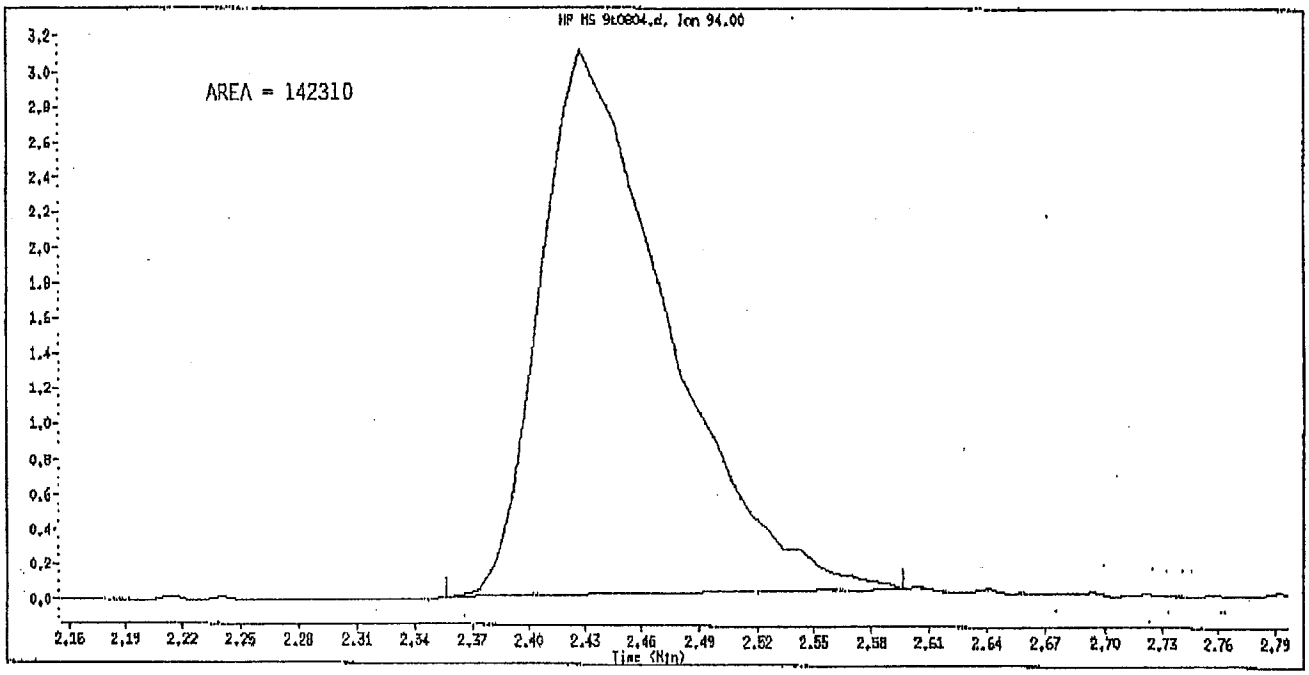
Column phase: Cap



Data File Name: 9t0804.d
Inj. Date and Time: 04-AUG-2005 19:42
Instrument ID: gc19.i
Client ID: LCD156604
Compound Name: Bromomethane
CAS #: 74-83-9
Report Date: 08/22/2005



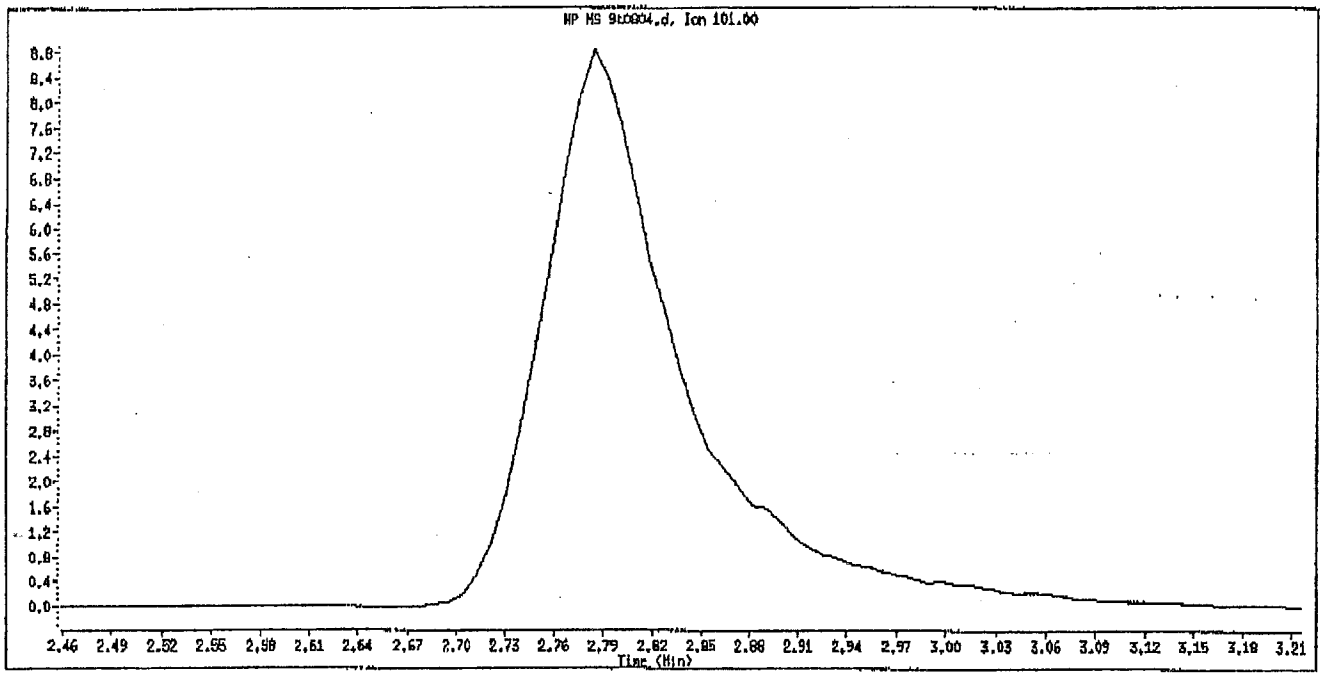
Original Integration



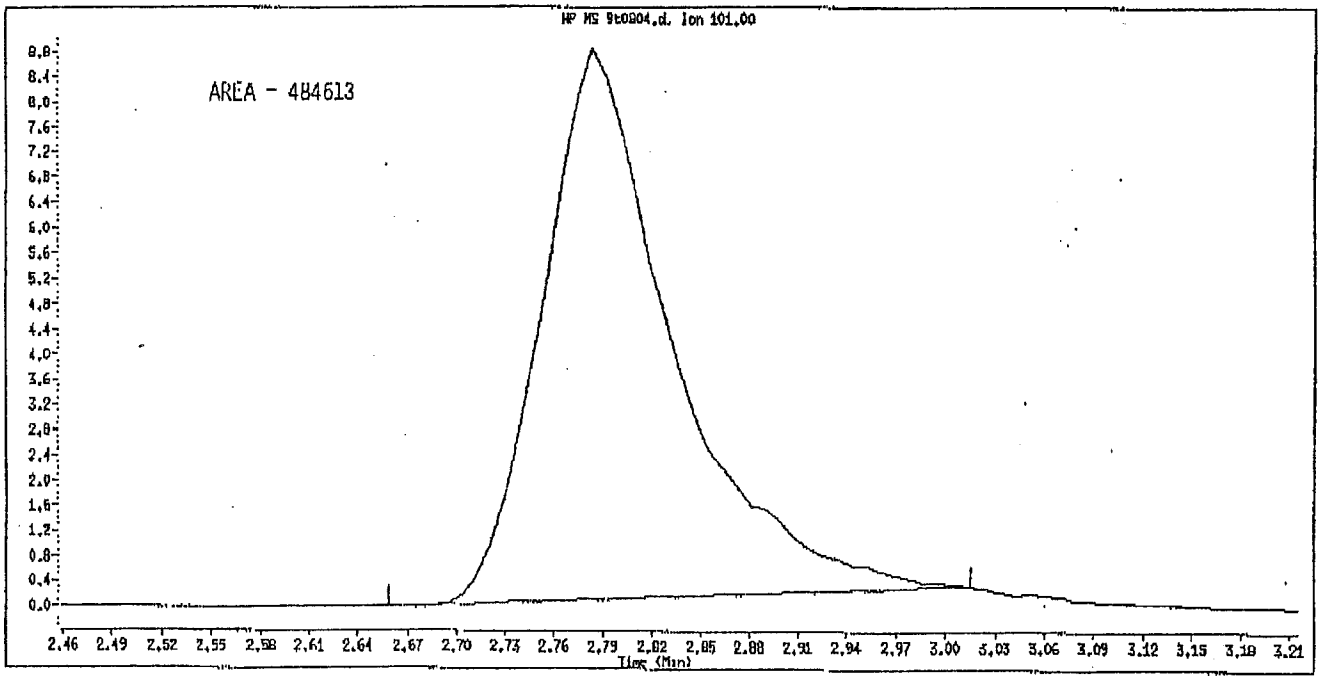
Manual Integration

Manually Integrated By: kobusm
Manual Integration Reason: M1 Peak missed 08/23/05

Data File Name: 9t0804.d
Inj. Date and Time: 04-AUG-2005 19:42
Instrument ID: gc19.i
Client ID: LCD156604
Compound Name: Trichlorofluoromethane
CAS #: 75-69-4
Report Date: 08/22/2005



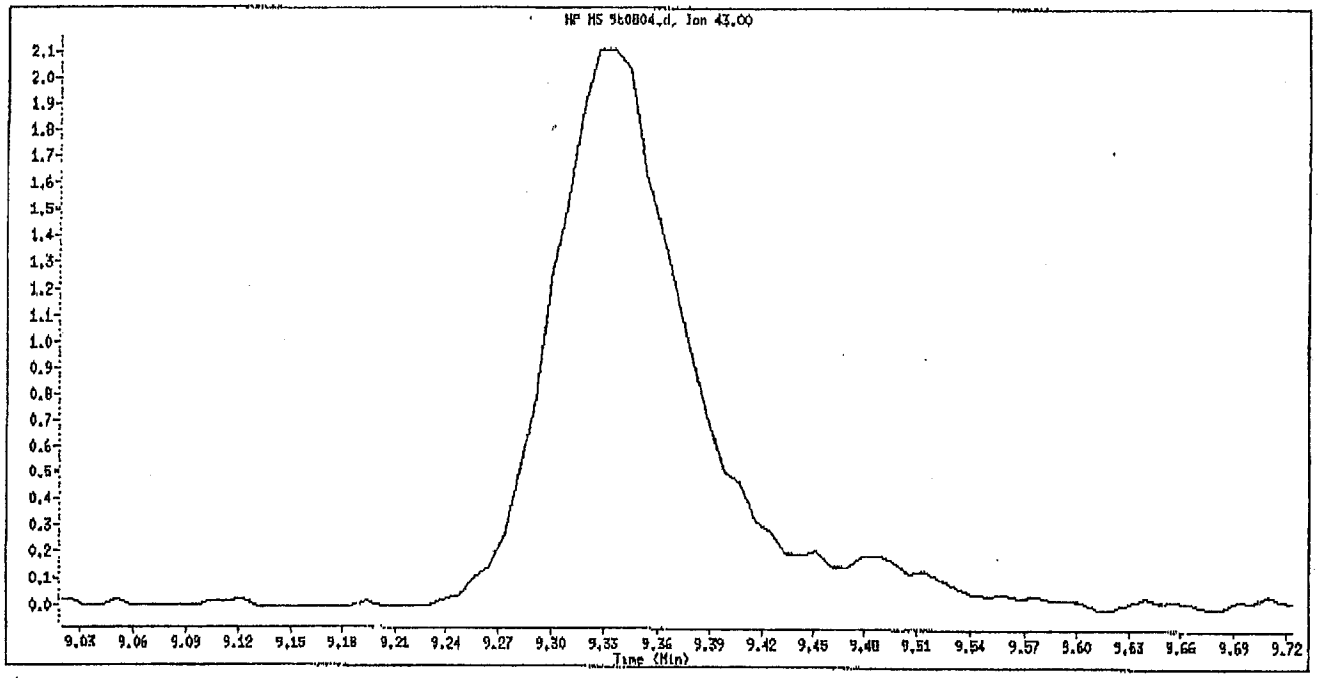
Original Integration



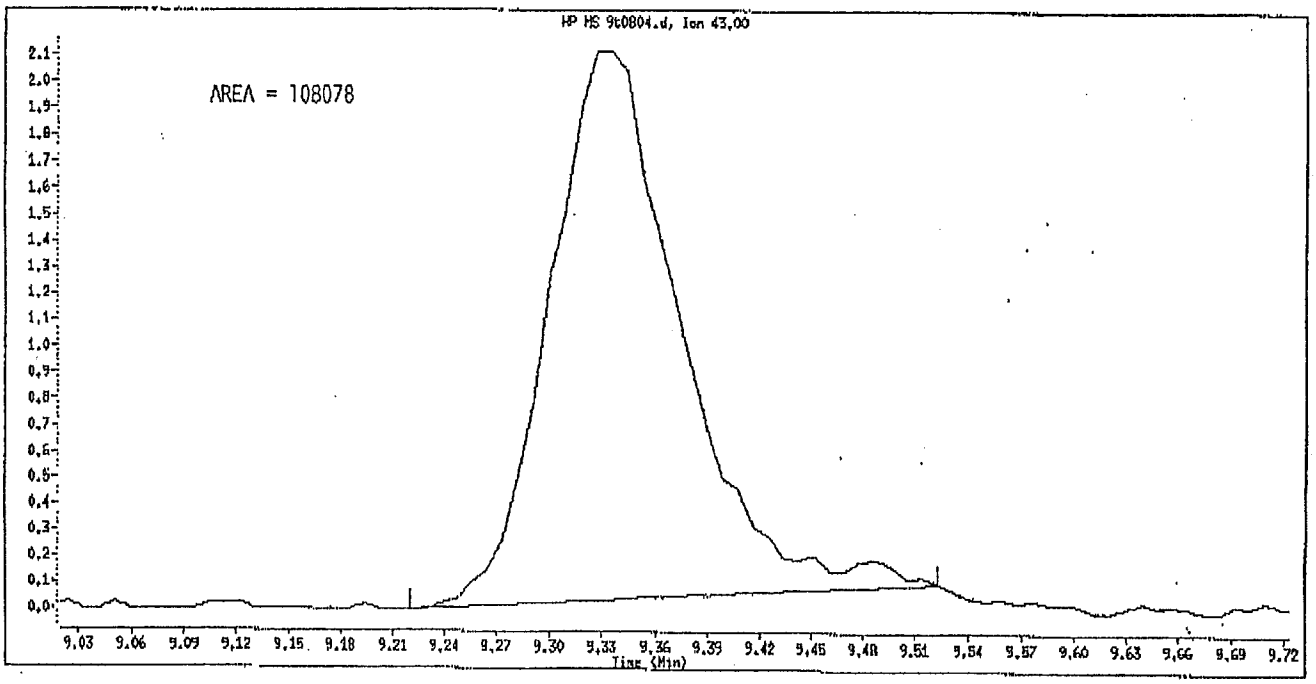
Manual Integration

Manually Integrated By: kobusm
Manual Integration Reason: M1 Peak missed GR 8/23/5

Data File Name: 9t0804.d
Inj. Date and Time: 04-AUG-2005 19:42
Instrument ID: gc19.i
Client ID: LCD156604
Compound Name: 4-Methyl-2-pentanone
CAS #: 108-10-1
Report Date: 08/22/2005



Original Integration



Manual Integration

Manually Integrated By: kobusm
Manual Integration Reason: MI Peak missed GC 8/23/05

VOA REPORT SW846 8260B SOILS

Data file : /var/chem/gcl9.i/080405.b/9t0804.d
Lab Smp Id: LCD Client Smp ID: LCD156604
Inj Date : 04-AUG-2005 19:42
Operator : GES Inst ID: gcl9.i
Smp Info : LCD
Misc Info : LCD,1.25,SOIL9,M
Comment : HP 5890 II/5972 MSD TEKMAR 3000 ARCHON AUTOSAMPLER
Method : /var/chem/gcl9.i/080405.b/Soil9.m
Meth Date : 22-Aug-2005 14:59 kobusm Quant Type: ISTD
Cal Date : 02-AUG-2005 12:09 Cal File: 9i0802e.d
Als bottle: 25 QC Sample: BSD
Dil Factor: 1.00000
Integrator: HP RTE Compound Sublist: 05ICAL1.sub
Target Version: 3.50
Processing Host: manatee

Concentration Formula: Amt * DF * Uf * 1/(Ws * (100-M)/100) * CpndVariable

Name	Value	Description
DF	1.00000	Dilution Factor
Uf	5.00000	ng unit correction factor
Ws	5.00000	Weight of sample extracted (g)
M	0.00000	% Moisture (not decanted)

Cpnd Variable Local Compound Variable

GC/8/23/15

Compounds	QUANT SIG MASS	RT	EXP RT	REL RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ug/L)	FINAL (ug/Kg)	
1 Dichlorodifluoromethane	85	1.742	1.740	(0.266)	378259	49.4719	49.472	
2 Chloromethane	50	1.947	1.945	(0.297)	173568	35.2803	35.280	
3 Vinyl chloride	62	2.063	2.060	(0.314)	172834	36.8059	36.806	
5 Bromomethane	94	2.428	2.434	(0.370)	142310	35.5169	35.517(M)	QR
6 Chloroethane	64	2.543	2.541	(0.388)	69766	31.7032	31.703	
7 Trichlorofluoromethane	101	2.784	2.781	(0.424)	484613	62.9275	62.927(M)	CIR
10 Trichlorotrifluoroethane	101	3.407	3.405	(0.519)	263031	31.3972	31.397	
11 1,1-Dichloroethene	96	3.425	3.422	(0.522)	160410	37.5830	37.583	
12 Acetone	43	3.647	3.654	(0.556)	21504	27.8302	27.830	
14 Carbon Disulfide	76	3.647	3.645	(0.556)	283651	20.6865	20.686	
18 Methylene chloride	84	4.119	4.117	(0.628)	179829	38.2390	38.239	
21 Methyl-tert-Butyl Ether	73	4.422	4.420	(0.674)	285601	49.4595	49.460	
22 trans-1,2-Dichloroethene	96	4.395	4.384	(0.670)	163919	41.0481	41.048	
24 1,1-Dichloroethane	63	4.992	4.989	(0.761)	293975	41.6174	41.617	

		Compounds	QUANT SIG MASS	RT	EXP RT	RLL RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ug/L)	CONCENTRATIONS FINAL (ug/Kg)
	25	Vinyl Acetate	43	5.090	5.078	(0.776)	158383	28.3902	28.390
M	29	1,2-Dichloroethene (total)	96				344061	83.5281	83.528
	30	cis-1,2-Dichloroethene	96	5.784	5.782	(0.882)	180142	42.4376	42.438
	31	2,2-Dichloropropane	77	5.731	5.728	(0.874)	268129	46.8672	46.867
	32	2-Butanone	43	5.882	5.862	(0.897)	39196	27.9548	27.955
	36	Bromochloromethane	128	6.113	6.102	(0.932)	143108	45.6549	45.655
	37	Tetrahydrofuran	42	6.167	6.165	(0.940)	23666	36.6290	36.629
	38	Chloroform	83	6.229	6.227	(0.950)	393944	48.5725	48.572
$	39	Dibromofluoromethane	113	6.461	6.449	(0.985)	489544	52.9062	52.906
*	40	Pentafluorobenzene	168	6.558	6.556	(1.000)	741052	50.2200	
	41	1,1,1-Trichloroethane	97	6.407	6.405	(0.977)	394313	54.1755	54.175
	44	1,1-Dichloropropene	75	6.647	6.636	(1.014)	308455	41.2297	41.230
	45	Carbon tetrachloride	117	6.585	6.583	(0.876)	496813	60.0745	60.074
$	47	1,2-Dichloroethane-d4	65	6.941	6.939	(0.923)	191332	62.8426	62.842
	48	Benzene	78	6.915	6.912	(0.919)	428782	41.0544	41.054
	49	1,2-Dichloroethane	62	7.048	7.037	(0.937)	182615	57.8694	57.869
*	52	1,4-Difluorobenzene	114	7.520	7.518	(1.000)	683749	50.2200	
	54	Trichloroethene	130	7.814	7.803	(1.039)	236645	47.2925	47.292
	56	1,2-Dichloropropane	63	8.161	8.150	(1.085)	176942	41.1329	41.133
	58	Dibromomethane	93	8.321	8.310	(1.107)	204518	47.4300	47.430
	59	Bromodichloromethane	83	8.526	8.524	(1.134)	433695	55.0855	55.085
	62	cis-1,3-Dichloropropene	75	9.122	9.120	(1.213)	257882	43.2820	43.282
	63	4-Methyl-2-pentanone	43	9.327	9.325	(1.240)	108078	40.7707	40.771(M)
$	64	Toluene-d8	98	9.398	9.396	(1.250)	594086	52.1520	52.152
	65	Toluene	92	9.487	9.476	(1.262)	301442	43.2927	43.293
	66	trans-1,3-Dichloropropene	75	9.879	9.868	(1.314)	214854	43.3342	43.334
	68	1,1,2-Trichloroethane	97	10.102	10.091	(1.540)	172124	43.4838	43.484
	69	Tetrachloroethene	166	10.155	10.153	(0.901)	300984	46.9814	46.981
	70	1,3-Dichloropropane	76	10.315	10.313	(0.915)	237074	44.6690	44.669
	71	2 Hexanone	43	10.422	10.402	(0.924)	70480	40.8478	40.848
	72	Dibromochloromethane	129	10.556	10.554	(0.936)	407354	53.0483	53.048
	73	1,2-Dibromoethane	107	10.707	10.696	(1.424)	287094	46.7310	46.731
*	74	Chlorobenzene-d5	117	11.277	11.275	(1.000)	531245	50.2200	
	75	1 Chlorohexane	91	11.277	11.275	(1.719)	217143	39.2280	39.228
	76	Chlorobenzene	112	11.312	11.310	(1.003)	411203	44.8782	44.878
	77	1,1,1,2-Tetrachloroethane	131	11.437	11.435	(1.014)	277629	53.7443	53.744
	78	Ethylbenzene	106	11.437	11.417	(1.014)	177460	44.6652	44.665
	79	p,m-Xylene	91	11.588	11.577	(1.028)	1005210	93.4697	93.470
	80	o-Xylene	91	12.096	12.085	(1.073)	501524	46.8047	46.805
	81	Styrene	104	12.132	12.120	(1.076)	382039	45.5307	45.531
M	82	Xylene (total)	100				1512734	139.507	139.51
	83	Bromoform	173	12.381	12.379	(1.098)	314167	53.0498	53.050
	84	Isopropylbenzene	105	12.559	12.548	(0.880)	613346	41.6164	41.616
$	86	p-Bromofluorobenzene	95	12.799	12.797	(1.135)	506382	55.6766	55.676
	87	1,1,2,2-Tetrachloroethane	83	13.040	13.028	(0.913)	254302	39.8009	39.801
	88	Bromobenzene	156	12.977	12.966	(0.909)	263387	45.2020	45.202
	89	1,2,3-Trichloropropane	110	13.093	13.082	(0.917)	68244	48.3760	48.376

8/23/5

	Compounds	QUANT SIG MASS	RT	EXP RT	REL RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ug/L)	CONCENTRATIONS FINAL (ug/Kg)
91	n-Propylbenzene	91	13.084	13.073	(0.916)	783420	42.4118	42.417
92	2-Chlorotoluene	91	13.218	13.207	(0.926)	611699	44.6079	44.608
93	1,3,5-Trimethylbenzene	105	13.324	13.322	(0.933)	531629	45.9057	45.906
94	4-Chlorotoluene	91	13.369	13.358	(0.936)	647295	43.6229	43.623
95	tert-Butylbenzene	119	13.716	13.714	(0.961)	585056	46.9727	46.973
97	1,2,4-Trimethylbenzene	105	13.805	13.794	(0.967)	540641	46.0516	46.052
98	sec-Butylbenzene	105	14.001	13.999	(0.981)	795236	44.0644	44.064
99	1,3-Dichlorobenzene	146	14.179	14.177	(0.993)	368798	42.4482	42.448
100	p-Isopropyltoluene	119	14.197	14.186	(0.994)	589437	43.4936	43.494
* 101	1,4-Dichlorobenzene-d4	152	14.277	14.275	(1.000)	348635	50.2200	
102	1,4-Dichlorobenzene	146	14.313	14.302	(1.002)	401589	41.6849	41.685
103	n-Butylbenzene	91	14.722	14.720	(1.031)	568738	40.3123	40.312
104	1,2-Dichlorobenzene	146	14.784	14.773	(1.036)	359608	43.8943	43.894
105	1,2-Dibromo-3-Chloropropane	75	15.746	15.753	(1.103)	62558	49.3534	49.353
108	1,2,4-Trichlorobenzene	180	16.636	16.625	(1.165)	274305	40.3038	40.304
109	Hexachlorobutadiene	225	16.779	16.768	(1.175)	271917	51.8465	51.846
110	Naphthalene	128	16.894	16.892	(1.183)	307415	43.7510	43.751
111	1,2,3-Trichlorobenzene	180	17.153	17.141	(1.201)	260475	43.4101	43.410

QC Flag Legend

M - Compound response manually integrated.

Appendix A.
Requirements for DOD QSM Version 3.0

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Organics (GC/MS)

QC Check	Definition	Purpose	Evaluation
Breakdown Check 8081A: Endrin, DDT 8270C: DDT	Analysis of s standard solution containing Endrin and DDT. Area counts of these compounds and their breakdown products are evaluated to assess instrument conditions.	To verify the inertness of the injection port because DDT and Endrin are easily degraded in the injection port.	If degredation of either DDT or Endrin exceeds method–specified criteria, corrective action must be taken before proceeding with calibration
Confirmation of positive results (organics only)	Use of alternative analytical techniques (another method, dissimilar column, or different detector such as MS detector) to validate the presence of target analytes identified	To verify the identification of an analyte	This is a required QC procedure. All positive results must be confirmed.
CCV	This verification of the initial calibration that is required during the course of analysis at periodic intervals. Continuing calibration applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models	To verify that instrument response is reliable, and has not changed significantly from the current ICAL	If the values for the analytes are outside the acceptance criteria, the initial calibration may not be stable. Results associated with out-of-control CCV results require reanalysis or flagging
Demonstrate Acceptable Analyst Capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision	To establish the analysts' ability to produce data of acceptable accuracy and precision	The average recovery and standard deviation of the replicate must be within designated acceptance criteria.
Duplicate Sample	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are taken and prepared and analyzed identically.	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intralaboratory analytical process for a specific sample matrix	To provide information on the heterogeneity of the sample matrix. The greater the heterogeneity of the matrix, the greater the RPD between the sample and the duplicate
ICAL	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method	To establish a calibration curve for the quantification of the analytes of interest	Statistical procedures are used to determine the relationship between the signal response and the know concentration of analytes of inte The ICAL must be successful before any samples or other QC check samples can be analyzed.
Internal Standards	A known amount of standard added to all standards and samples as a reference for evaluating and controlling the precision and bias of the applied analytical method	To verify that the analytical system is in control	Any sample associated with out-of-control results must be reanalyzed.
LCS containing all analytes required to be reported	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern.	To evaluate method performance by assessing the ability of the lab/analyst to successfully recover the target analytes from a control (clean) matrix.	This is a required QC Check. The inability to achieve acceptable recoveries in the LCS indicate problems with the accuracy/bias of the measurement system.
MS	A sample prepared by adding a know amount of targeted analyte(s) to an aliquot of a specific environmental sample	To assess the performance of the method as applied to a particular matrix	The lack of acceptable recoveries in the matrix spike often points to problems with the sample matrix. One test of this is a comparison to the LCS recoveries. If the corresponding LCS recoveries are within acceptable limits, a matrix effect is likely. The lab should not correct for recovery; only report the results of the analyses and the associated MS results and indicate that the results from these analyses have increased uncertainty
MSD	A 2nd replicate MS prepared in the lab, spiked with an identical, known amount of targeted analyte(s), and analyzed to obtain a measure of the precision of the recovery for each analyte	To assess the performance of the method as applied to a particular matrix and provide information of the homogeneity of the matrix.	When compared to the MS, the MSD will provide information on the heterogeneity of the sample matrix.

Table B-1 Cont.			
QC Check	**Definition**	**Purpose**	**Evaluation**
MDL Verification Check	A low-level spike taken through the prep and analytical steps at approximately 2x the MDL used to verify that the laboratory can detect analytes at the calculated MDL	To validate the MDL on an ongoing basis	If the MDL verification check fails, reprep/reanalyze at a higher level to set a higher MDL or the MDL study must be repeated.
MB	A sample of a matrix similar to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results.	To assess background interferences or contamination in the analytical system that might lead to high bias or false positive data.	This QC is used to measure lab accuracy/bias. The MB could indicate whether contamination is occurring during sample prep and analysis. If analytes are detected > ½ RL, reanalyze or B-Flag results for all samples in prep batch. For common lab contaminants, no analytes detected > RL. See DoD Box D-5; & Sec. D.1.1.1
MDL Study	The process to determine the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.	MDLs must be established prior to sample analysis. The RL or LOQ is at least 3x the MDL. Used in combination with the MDL verification check to validate the MDL on an ongoing basis.
RT window position establishment for each analyte (chromatographic methods only)	Determination of the placement of the RT window (start/stop time) of each analyte or group of analytes as it elutes through the chromatographic column so that analyte identification can be made during sample analysis. This is done during the initial calibration	To idendify analytes of interest	Incorrect window position may result in false negatives, require additional manual integrations, and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified.
RT window verification for each analyte (chromatographic methods only)	A standard is used to verify that the width and position of the RT windows are valid so that accurate analyte identification can be made during sample analysis	To minimize the occurance of both false positive and false negative results at each calibration verification.	The peaks from the standard used are compared to the RT window established during the ICAL to verify that the analytes of interest still fall within the window.
Second source calibration verification	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration	The concentration of the 2nd source calibration verification, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. This independent verification of the ICAL must be acceptable before sample analysis can begin.
Surrogate spike (organic analysis only)	A pure substance with properties that mimic the analyte of interest. Surrogates are compounds unlikely to be found in environmental samples to evaluate analytical efficiency by measuring their % Recovery.	To assess the ability of the method to successfully recover specific non-target analytes from an actual matrix.	Whereas the MS is normally done on a batch-specific basis, the surrogate spike is done on a sample-specific basis. Taken with the information derived from other spikes (LCS; MS), the bias in the analytical system can be determined.
Tuning (MS methods only)	The analysis of a standard compound to verify the mass spectrometer meets standard mass spectra abundance criteria prior to sample analysis	To verify the proper working of the mass spectrometer	Proper tuning of the mass spectrometer must be verified prior to sample analysis

Notes:

1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-3: Organic Analysis by GC/MS - Methods 8260 and 8270

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
IDOC	Per Instrument/Analyst	DoD acceptance criteria if available; otherwise method specific criteria	Correct / Repeat for those analytes which failed criteria	NA
MDL	Annually or quarterly MDL Checks performed	40 CFR 136B; MDL verification checks must produce a signal at least 3x the instrument's noise level.	Run MDL check at higher level and set MDL higher or reconduct MDL study	NA
Tuning	Prior to calibration and every 12 hours during sample analysis	Refer to method specific ion criteria	Retune instrument and verify. Rerun affected samples	NA
Breakdown check DDT (8270C only)	Daily prior to analysis of samples	Degradation $\leq$ 20% for DDT (Benzidine & PCP should be present at their normal response and no peak tailing should be observed)	Correct problem then repeat breakdown check	NA
ICAL	Initial 5-point calibration prior to sample analysis	1. Average RF for SPCCs: VOCs - $\geq$ 0.30 for Chlorobenzene and 1,1,2,2-tetrachloroethane, $\geq$ 0.1 for chloromethane, bromoform, and 1,1-dichloroethane SVOCs - $\geq$ 0.050 2. RSD for RFs for CCCs: VOCs and SVOCs - $\leq$ 30% and one option below. **Option 1:** RSD for each analyte $\leq$ 15% **Option 2:** linear least squares regression: $r \geq 0.995$ **Option 3:** non-linear regression: Coefficient of determination (COD) $r^2 \geq 0.99$ (6 points shall be used for 2nd order, 7 points shall be used for 3rd order)	Correct problem then repeat initial calibration	NA
2nd Source calibration verification	Once after each initial calibration	Value of 2nd source for all analytes within $\pm$ 25% of expected value	Correct problem and verify 2nd source standard. Rerun, if that fails, correct problem and repeat ICAL	NA
RT window position establishement for each analyte	Once per ICAL	Position shall be set using midpoint standard of the initial calibration curve	NA	NA
Evaluation of Relative RT (RRT)	With each sample	RRT of each target analyte in each calibration standard within $\pm$ 0.06 RRT units	Correct problem, then rerun ICAL	NA
Calibration verification (CV)	Daily, before sample analysis, and every 12 hours of analysis time	1. Average RF for SPCCs: VOCs - $\geq$ 0.30 for Chlorobenzene and 1,1,2,2-tetrachloroethane, $\geq$ 0.1 for chloromethane, bromoform, and 1,1-dichloroethane SVOCs - $\geq$ 0.050 2. %Difference for CCCs: VOCs and SVOCs - $\leq$ 20% D (Note: D = difference when using RFs or drift when using least squares regression or non-linear calibration) All calibration analytes must be within 20% D, with no individual analytes (except CCC's) > 25% D (DoD Version 2.2)	Correct problem, rerun CV, if fails, repeat ICAL (Data associated with an unacceptable CCV may be fully usable under the following conditions: 1. CCV (high bias) and samples ND, then raw data may be reported with appropriate flag 2. CCV (low bias) and samples exceed maximum regulatory limit/decision level (DoD Box 60: Project specific permission from appropriate DoD personnel is required to report data generated from a run with noncompliant CCV.)	Apply J-flag to all results associated with the analytical batch for all analytes > 20%D and < 25% D. Identify in case narrative analytes > 20% D. (DoD Version 2.2) Apply Q-flag if no sample material remains and analyte exceeds criteria
Internal Standards verification	In all field samples and standards	RT $\pm$ 30 seconds from RT of the midpoint standard in the ICAL EICP area within -50% to +100% of ICAL midpoint standard	Inspect mass spectrometer and GC for malfunctions. Reanalysis of samples analyzed while system was malfunctioning is mandatory	Apply Q-flag to analytes associated with the non-compliant IS.
MB	One per prep batch	No analytes detected > ½ RL For common lab contaminants, no analytes > RL	Correct problem, then see criteria in box D-5; if required, reprep/reanalyze MB and all associated samples	Apply B-flag to all results for the contaminated analyte for all samples in the associated prep batch

Table B-3 cont.				
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**
LCS (containing all analytes to be reported)	One LCS per prep batch	DoD specified QC criteria, if available	Correct problem, reprep/reanalyze the LCS and all samples in the associated prep batch for all failed analytes, if sufficient sample is available	Apply Q-flag to specific analyte(s) in all samples in the prep batch.
MS	One per prep batch per matrix	For matrix evaluation, use DoD specified QC criteria for LCS	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample
MSD or Sample Duplicate	One per prep batch per matrix	RPD $\leq$ 30% (between MS and MSD or sample and sample duplicate)	Examine the project-specific DQOs. Contact client for additional corrective action measures.	Apply J-flag to specific analyte(s) in the parent sample
Surrogate	All field and QC samples	DoD specified QC criteria if available, otherwise method specific criteria or lab's own in-house criteria	For QC and field samples, correct problem, reprep/reanalyze all failed samples in the associated prep batch if sufficient sample material is available.	Apply J-flag for specific analyte(s) in all field samples collected from the same site matrix as the parent. Apply Q-flag to QC samples for specific analyte(s)
Results reported between LOD and LOQ			Apply J-flag to all results between LOD (MDL) and LOQ (RL)	
Manual Integration	When manual integrations are performed	Raw data shall include a complete audit trail for those manipulations, raw data output showing the results of the MI (i.e., chromatograms of manually integrated peaks), and notation of rationale, date, and signature/initials of person performing manual operation.		Apply M-flag to MI data

Notes:

1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

STL Chicago
STANDARD OPERATING PRACTICE (SOP) CHANGE FORM

Original SOP Number/Revision #: USP-3000 Rev. 14 Last Mod ID (circle): NA/ A
SOP Title: Metals Digestion by SW-846 3000 Series
Affected SOP Section Number(s): Sections 1.0 and 7.6
Effective Date: 06/07/06

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Revision Number with Mod ID:

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. **Append this form to the front of the SOP copy.**

1. Reason for SOP Change: Corrective Action Response for NC Audit April 3-4, 2006

2. Summary of Procedure Change (circle to indicate if there are attachments to this form: No / Yes: # pages attached = _)

During the audit it was noted that the laboratory is required to prepare NC WW/GW samples using Standard Methods 3030C 20th Edition. The current SOP will be edited upon the next revision to document that all such samples will be prepared according to this method. In the interim, this SOP change form serves to document the change in procedure. The preparation will be outlined in Section 7.6. The proper reference to Standard Methods will be added to Section 1.0. All other methods will remain as referenced to SW-846.

Note: As stated in the Standard Operating Procedure, client contractual requirements/QAP's/Project and/or Program Requirements may stipulate specific preparation methods. In cases such as these, those requirements will supersede.

Initiated/Reviewed By: Name/Date — 05/31/06

N/A
Initiated/Reviewed By: Name/Date

Approval Signature/Date: Section Manager — 5/31/06

Approval Signature/Date: QA Manager or Designee — 5/31/06

STL Chicago
STANDARD OPERATING PRACTICE (SOP) CHANGE FORM

Original SOP Number/Revision #: USP-3000 Rev 14 Last Mod ID (circle): NA (A)
SOP Title: Sample Preparation by SW-846 3000 Series
Affected SOP Section Number(s): Section 1.0 Scope and Application
Effective Date: October 5, 2006

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1. Reason for SOP Change: Inclusion of ICP-MS as reference

2. Summary of Procedure Change (circle to indicate if there are attachments to this form: (No) Yes: # pages attached = _)

Section 1.0 Table will be edited to include reference to ICP-MS for the following possible extraction procedures:

EPA 3005A, EPA 3010A and EPA 3050B

Maureen S. Kinney 10/05/06
Initiated/Reviewed By: Name/Date

N/A
Initiated/Reviewed By: Name/Date

Lisa Odesho 10/5/06
Approval Signature/Date: Section Manager / Supervisor

Teresa A. Preston 10/5/06
Approval Signature/Date: QA Manager or Designee

SOP No.	Revision No.	Date	Page
USP-3000	14	03/16/06	1 of 15

TITLE: SAMPLE PREPARATION
Metals Digestion by SW-846 3000 Series

Updated by:	Signature:	Date:
Carla Bonner Analyst, Metals Department	Carla Bonner	3-16-06

Approved by:	Signature:	Date:
Jodi L. Gromala Supervisor, Metals Dept.	Jodi Gromala	3-14-06
David W. Mazur Env. Health & Safety Coor.	DW Mz	3/16/06
Terese A. Preston Quality Manager	Terese A. Preston	3/16/06

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) outlines the guidelines for the preparation of wastewaters, extracts, wastes and soil samples for metals analysis by Trace Inductively Couples Argon Plasma (ICP) and Graphite Furnace AA (GFAA). This SOP was written using the following methods of SW-846, Third Edition:

Method	Description
3005A	Surface and ground waters for analysis by Trace ICP.
3010A	Waters and extracts for analysis by Trace ICP.
3020A	Waters and extracts for analysis by GFAA (excluding As and Se).
3020A Modified	Waters and extracts for analysis by GFAA (including As and Se w/ H_2O_2).
3050B	Soil and waste samples for analysis by Trace ICP or GFAA.
7060A	Waters for As by GFAA.
7740	Waters for Se by GFAA.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

Not Applicable. Refer to the analytical SOPs.

1.1.2 Reporting Limits

Not Applicable. Refer to the analytical SOPs.

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.2 Summary of Method

Water and soil samples are digested with nitric acid, hydrochloric acid and/or hydrogen peroxide to produce digestates that are in the correct acid media for analysis by the Trace ICP or GFAA.

2.0 INTERFERENCES

Matrix interferences are usually not present for the digestion process. Analytical matrix interferences may be apparent during the instrumental analysis of the digestates. The type of interferences for the instruments are discussed in the appropriate SOPs.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

- Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.
- Acid vapor can be dangerous. Work in a well ventilated area (i.e., fume hood).
- Hydrogen peroxide (H_2O_2) is a strong oxidizer and is corrosive. The digestion must be cooled sufficiently before the addition of H_2O_2 to avoid a reaction and possible violent effervescence, or boiling over of the digestion. A splash/splatter hazard is possible and a face shield should be worn

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE:** This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm-TWA	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

- Top loading balance
- Hot plate (w/ thermometer)
- Hot Block w/ digestion vessels (w/ thermometer)
- 250 mL beakers
- 100 mL graduated cylinders
- Whatman No. 541 filter paper
- Funnels
- 100 & 50 mL Class A volumetric flasks
- Fume hood(s)
- Eppendorf Pipettes
- Watch glasses (ribbed & non-ribbed)
- Filters and plunger apparatus
- 100 & 50 mL digestate vessels (which are checked to ensure volume markings are within 2.5% Tolerance).
- 100 mL Snap-Cap containers for digestates (which are checked to ensure volume markings are within 2.5% Tolerance).

5.0 REAGENTS AND STANDARDS

5.1 Reagents

- Concentrated Nitric Acid (Instra Pure)
- Concentrated Hydrochloric Acid (Instra Pure)
- 30% Hydrogen Peroxide Solution

Purchased from a chemical vendor.

- Life of Reagent: Specified by the Manufacturer, usually 1 year.
- Storage Requirements: Acid Cabinet

5.2 Standards

5.2.1 Trace ICP and GFAA Intermediate Standards

These standards are prepared from multi-element solutions purchased from vendors. Single element spikes may be used if needed. These solutions expire 1-year from the date of receipt.

Standard	Preparation
Trace ICP Spike Solution	• Add ~400 mLs of Milli-Q water to a 1-L Class A volumetric flask. • Add 100 mLs each of HP1381-A-500, HP1381-B-500 and HP1381-C-500; • Add 9 mLs of 1,000 ppm Se; • Add 8 mLs of 1,000 ppm Pb; • Add 6 mLs of 1,000 ppm As; • Add 5 mLs of 1,000 ppm Tl; and • Add 40 mLs of InstraPure nitric acid. • Swirl to mix; Dilute to volume with Milli-Q water. Life of Standard: Expiration date of the earliest expiring standard. Storage Requirements: None.
GFAA Spike Solution	• Add ~500 mLs of Milli-Q water to a 1-L Class A volumetric flask. • Add 20 mLs of nitric acid; • Add 10 mLs of STL-CLP-60R • Swirl to mix. Dilute to volume with Milli-Q water. Life of Standard: Expiration date of the earliest expiring standard. Storage Requirements: None.
GFAA Ag Spike Solution	• Add ~500 mLs of Milli-Q water to a 1-L Class A volumetric flask. • Add 20 mLs each of nitric acid and hydrogen peroxide. • Add 2 mLs of 1000 ppm Ag. • Swirl to mix. Dilute to volume with Milli-Q water. Life of Standard: As defined by the manufacturer. Storage Requirements: None.

Refer to Appendix A for the individual element concentrations within the spiking solutions. Matrix spikes for TCLP extracts are added after filtration of the TCLP extract and before preservation. Refer to SOP No. USP-1311.

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

QC Indicator	Preparation	Frequency
Method Blank (MB)	For soil sample batches, use 100 mLs of Milli-Q water. [1]	1 per 20 or fewer samples.
	For water sample batches, use 50 mLs of Milli-Q water.	1 per 20 or fewer samples.
Matrix Duplicate (MD) [2]	Aliquot of the same field sample that is digested independently.	1 per 20 or fewer samples.
Laboratory Control Sample (LCS) [3]	For soil sample batches, use 100 mLs of Milli-Q water and spike as listed below. [1 4]	1 per 20 or fewer samples.
	For water sample batches, use 50 mLs of Milli-Q water and spike as listed below. [4]	1 per 20 or fewer samples.
Matrix Spike (MS); MS Duplicate (MSD) [2]	Aliquot of the same field sample that is spiked as listed below [3] and digested independently.	1 per 20 or fewer samples.

[1] For those programs, clients and projects mandating the use of a 'soil' matrix for the preparation of Soil MB's and LCS's (including all DoD and NFESC projects), Teflon Stands will be incorporated.
[2] The sample selection for MS/MSD/MD is rotated among client samples so that various matrix problems may be noted and/or addressed.
[3] LCS Duplicate (LCD) is performed when requested by the client, contract or QAP.

[4] The LCS and MS/MSD are spiked with a known amount of analyte and processed through the digestion procedure. The spiking procedure is as follows:

Instrument	Waters Spike Volume	Soils Spike Volume
Trace ICP	0.5 mL of Trace ICP Intermediate Spiking Solution.	1 mL of Trace ICP Intermediate Spiking Solution.
GFAA	0.5 mL of GFAA Intermediate Spiking Solution.	1 mL of GFAA Intermediate Spiking Solution.

Refer to Appendix A for the individual element concentrations within the spiking solutions. Matrix spikes for TCLP extracts are added after filtration of the TCLP extract and before preservation. Refer to USP-1311.

7.2 Sample Preservation and Storage

Matrix	Holding Time	Preservation
Waters	180 days	HNO_3, pH <2; Cool 4 ± 2°C
Soils	180 days	Cool 4 ± 2°C

7.2.1 Sample Handling Procedures (Other than Soils / Waters)

Matrix	Description
Wipes	The entire wipe is digested with results reported as ug/wipe.
Paint Chips	Care is taken to remove the paint from the substrate. The chips are then cut and ground into a fine powder. Sample size is 0.1 to 0.5 grams.
Solids *	Dried and ground with a mechanical crusher.

*Bricks, wood, etc..

7.3 Sample Preparation

- Since the pH is checked by the sample custodian at sample receipt, the digestion analysis will check the pH at random and/or if the analyst has a reason to suspect that the sample may not be preserved.
- The start and end temperature of the hot plate or hot block digestion is documented within LIMS.

NOTE: The LCS and MB must be filtered when analyzed with dissolved metals that are filtered in the laboratory (unpreserved samples).

7.4 Calibration / Standardization

Not Applicable.

7.5 Preventive Maintenance

- To minimize contamination during sample preparation, the fume hoods and counter areas must be kept clean and free of dust.
- The digestion hoods are cleaned on a regular basis (a minimum of once a month) and documented within the hood maintenance log.

7.6 Sample Digestion

7.6.1 Method 3005A

- Transfer 50 mLs of the well-mixed (homogenized) sample into a 50 mL digestion vessel.
- Add 1 mLs of InstraPure nitric acid and 2.5 mLs of InstraPure hydrochloric acid.

- Cover the vessel with a ribbed watch glass and heat on a preheated hot block at 90-95°C until the volume has been reduced to 10-15 mLs.
- Remove the vessels from the hot block and allow to cool.
- Fill to a 50 mL final volume in the digestion vessel with Milli-Q water and filter using the plunger apparatus.
- The sample is now ready for analysis.

NOTE: When using the Hot Plates, all volumes remain the same in the 250 mL beaker. When filtering, wash down the sides of the beaker with Milli-Q water and filter into a 50 mL volumetric flask through Whatman 541 filter paper. Dilute the sample to a final 50 mL volume using Milli-Q water.

7.6.2 Method 3010A

- Transfer 50 mLs of the well-mixed (homogenized) sample into a 50 mL digestion vessel.
- Add 1.5 mLs of InstraPure nitric acid.
- Cover the vessel with a ribbed watch glass and place on a preheated hot block set at 90-95°C.
- Evaporate the sample down to a low volume – just enough to cover the bottom of the vessel. **The sample should not boil or any portion of the vessel bottom allowed to go dry.**
- Remove the vessel from the hot block and allow to cool.
- Add another 1.5 mL portion of InstraPure nitric acid.
- Cover the vessel with a non-ribbed watch glass and return to the hot block to allow a gentle reflux to occur.
- Continue to add InstraPure nitric acid as necessary, until the digestion is complete (no change in appearance with continued refluxing).
- Uncover and evaporate to a low volume, not allowing any part of the vessel to go dry.
- Remove the vessels from the hot block and allow to cool.
- Add 2.5 mLs of InstraPure hydrochloric acid and 2.5 mLs of Milli-Q water.
- Warm the vessel for another 15 minutes to dissolve any precipitate.
- Remove from hot block and allow to cool.
- Fill to a 50 mL final volume in the digestion vessel with Milli-Q water and filter using plunger apparatus.
- The sample is now ready for analysis.

NOTE: When using the Hot Plate, the volume remains the same in a 250 mL beaker. When filtering wash down the sides of the beaker with Milli-Q water and filter the sample into a 50 mL volumetric flask through Whatman 541 filter paper. Dilute to the 50 mL final volume with Milli-Q water.

7.6.3 Method 3020A

- Transfer 50 mLs of the well-mixed (homogenized) sample into a 50 mL digestion vessel.
- Add 1.5 mLs of InstraPure nitric acid.
- Cover the vessel with a ribbed watch glass and place on a preheated hot block set at 90-95°C.
- Evaporate the sample down to a low volume – just enough to cover the bottom of the vessel. **The sample should not boil or any portion of the vessel bottom allowed to go dry.**
- Remove the vessels from the hot block and allow to cool.
- Add another 1.5 mL portion of InstraPure nitric acid.
- Cover the vessel with a non-ribbed watch glass and return to the hot block to allow a gentle reflux to occur.
- Continue to add InstraPure nitric acid as necessary, until the digestion is complete (no change in appearance with continued refluxing).
- Uncover and evaporate to a low volume, not allowing any part of the vessel to go dry.
- Remove the vessel from the hot block and allow to cool.
- Add 5 mLs of Milli-Q water and continue warming for 10-15 minutes to dissolve any precipitates.
- Remove from the hot block and allow to cool.
- Fill to a final 50 mL volume in the digestion vessel with Milli-Q water and filter using plunger apparatus.
- The sample is now ready for analysis.

NOTE: When using the Hot Plate, all volumes remain the same in 250 mL beaker. When filtering wash down the sides of the beaker with Milli-Q water and filter the sample into a 50 mL volumetric flask through Whatman 541 filter paper. Dilute to the 50 mL final volume with Milli-Q water.

7.6.4 Method 3020A Modified

This method is equivalent to Method 3020A, however, 1 mL of hydrogen peroxide is added to the sample with the initial 1.5 mLs of nitric acid.

7.6.5 Method 3050B

- Weigh out 1.00 – 2.00 grams of the well-mixed sample into a 250 mL beaker. The exact weight is recorded in the LIMS digestion spreadsheet.
- For samples with a high liquid content, more sample may be used as long as the digestion is complete.

NOTE: When using the hot blocks, soils are generally weighed to 1.00-1.20 grams due to the size of the digestion vessels. All other volumes are the same as for the hot plate/beaker digestions.

Add 5 mLs of InstraPure nitric acid and 5 mLs of Milli-Q water.

- Cover the beaker with a non-ribbed watch glass and place on a preheated hotplate set at 90-95°C for 15 minutes without boiling.
- Remove the beaker from the hot plate and allow to cool.
- Add 5 mLs of InstraPure nitric acid and reflux for 30 minutes.
- If brown fumes are generated, repeat this last step until no brown fumes are generated indicating complete reaction with the nitric acid.
- Allow the solution to evaporate to a low volume – just enough to cover the bottom of the beaker. **Do not allow the sample to boil.**
- Remove the beaker from the hot plate and allow to cool.
- Add 2 mLs of Milli-Q water and 3 mLs of 30% hydrogen peroxide.
- Cover the beaker and heat until the reaction is complete.
- Remove the beaker from the hot plate and allow to cool.
- Continue to add 30% hydrogen peroxide in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance in unchanged. **Do not add more than a total of 10 mLs of hydrogen peroxide.**
- Cover the sample with a ribbed watch glass and heat until the volume has been reduced to ~5mLs or heat at 90-95°C for 2-hours without boiling.
- Maintain a covering of solution on the bottom of the beaker at all times.

****

If the sample is being analyzed by the Trace ICP:

- Allow the sample to cool.
- Add 10 mLs of InstraPure hydrochloric acid.
- Place the beaker on the hot plate and heat for 15 minutes without boiling.
- Remove the beaker from the hot plate and allow to cool.
- Wash down the sides of the beaker with Milli-Q water and filter into a 100 mL snap-cap container through Whatman 541 filter paper.
- Dilute the sample to the 100 mL mark in a snap-cap container.
- The sample is now ready for analysis.

If the sample is being analyzed by GFAA:

- Allow the sample to cool.
- Wash down the sides of the beaker with Milli-Q water and filter into a 100 mL Class A volumetric flask through Whatman 541 filter paper.
- Dilute the sample to the 100 mL snap-cap container through Whatman 541 filter paper.
- The sample is now ready for analysis.

7.6.6 Methods 7060A / 7740

- Transfer 50 mLs of the well-mixed (homogenized) sample into a 50 mL digestion vessel.
- Add 1 mL of Hydrogen Peroxide and 0.5 mL of InstraPure nitric acid.
- Place the vessel on a preheated hot block set at 90-95°C.
- Evaporate the sample down to a volume slightly less than 25 mLs.
- Remove the samples and allow to cool.
- Fill to a final 50 mL volume in the digestion vessel with Milli-Q water and filter using the plunger apparatus.
- The sample is now ready for analysis.

NOTE: When using the Hot Plate, all volume remains the same in a 250 mL beaker. When filtering, wash down the sides of the beaker with Milli-Q water. Filter the sample through Whatman 541 filter paper into a 50 mL volumetric flask. Dilute to volume with Milli-Q water.

7.7 Documentation

7.7.1 LIMS Digestion Spreadsheets

Sample digestion and standard traceability are documented within the LIMS spreadsheets. The spreadsheets must be completed for each days work. The time of digestion and temperature of the hot plate/block must be recorded. Refer to Appendix B for an examples of the GFAA and Trace ICP digestion spreadsheets.

7.7.2 Traceability of Standards

Custom made and single element stock standard solutions which are traceable to NIST or EPA are purchased. Upon receipt, each standard is entered into the LIMS database and is issued a unique source ID#. The manufacturer, lot #, date received, expiration date, and the initials of the analyst are also entered.

8.0 QUALITY CONTROL

8.1 QC Summary

QC Standard	Indicator
Method Blank (MB)	Examined to determine if there was any contamination introduced during the digestion process.
Laboratory Control Sample (LCS)	Used to determine the completeness of the digestion process. The accuracy is measured by the percent recovery (%R) of each standard.
Matrix Duplicate (MD)	Demonstrate analytical precision and is reported as Relative Percent Difference (RPD).
Matrix Spike (MS) / MS Duplicate (MSD)	Used to demonstrate analytical accuracy and is reported as % recovery.

8.2 Corrective Action

A Corrective Action Report (CAR) will be filled out by the analyst anytime there is a deviation from the routine preparation procedures, as outlined within this SOP. This includes, but is not limited to: limited sample volume, sample loss due to spills, extremely vigorous reactions, spiking issues or any other issues that may occur during the preparatory procedure. The Section Manager will review the CAR and document any corrective action needed at that time. All Analysis 'out-of-control' situations are identified as indicated in the supporting analytical SOP's proper.

9.0 DATA ANALYSIS AND CALCULATIONS

Not Applicable.

10.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by the Method

- Waste from this procedure will enter the "Corrosive Wastewater" wastestream.

11.0 METHOD PERFORMANCE CRITERIA

Refer to sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0.

13.0 ATTACHMENTS

Appendix A. Metals Digestion Standard Spike Concentrations
Appendix B. Example: GFAA and Trace ICP LIMS Digestion Spreadsheets

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Historical File:

Revision 00: 08/15/91
Revision 01: 03/16/93
Revision 02: 08/20/93
Revision 03: 01/20/94
Revision 04: 11/22/95
Revision 05: 02/18/97
Revision 06: 10/07/97
Revision 07: 10/16/97
Revision 08: 03/31/99
Revision 09: 05/05/00
Revision 10: 07/06/01
Revision 11: 01/09/03
Revision 12: 01/07/04
Revision 13: 02/11/05
Revision 14: 03/16/06

Reasons for Change, Revision 14:

- Annual Review – Changed reference from LabNet to LIMS
- Addition of Corrective Action steps to Section 8.2
- Table 7.1 amended to reflect addition of Teflon Strands

U:\QC\SOP\SP\USP-3000.DOC

Appendix A.

Metals Digestion Standard Spike Concentration

Trace-ICP

Vendor	Stock Name	Elements	Conc. (mg/L)
Environmental Express	HP1381-A-500	Al, Ba	2,000
		Ca, Mg, K, Na	10,000
	HP1381-B-500	Se	10
		Pb	20
		As	40
		Tl, Be, Cd	50
		Cr	200
		Cu	250
		Co, Ni, Li, V, Bi, Mn, Zn	500
		B, Fe, Sr	1,000
	HP1381-C-500	Ag	50
		Sb, P	500
		Mo, Sn, Ti	1,000
		Si	5,000
Inorganic Ventures	Single Element Standard	As	1,000
		Pb	1,000
		Se	1,000
		Tl	1,000

GFAA

Vendor	Stock Name	Elements	Conc. (mg/L)
Inorganic Ventures	STL-CLP-60R	Sb, Tl	500
		As	400
		Cr, Cu, Pb	200
		Se	100
		Cd	50
	Single Element Standard	Ag	1,000

TCLP (MS)

Vendor	Stock Name	Elements	Conc. (mg/L)
Inorganic Ventures	STL-TCLP-1A	Hg	25
		Cu	25
		Zn, Ni	50
		Cd, Se, Ag	100
		Cr, As, Pb	500
	Single Element Standard	Ba	10,000

Appendix B.

Example: LIMS Digestion Spreadsheets

Metals/Inorgar s Analysis Sheet

(To Accompany Samples to Instruments)

Batch Number: 500-885 Analyst: Cann, Randall Batch Open: 3/15/2006 6:15:00PM

Method Code: 500-3010A-500 Batch End: 3/15/2006 6:15:00PM

Acid Digestion of Aqueous Samples and Extracts for Total Metals

	Input Sample Lab ID (Analytical Method)	SDG	Matrix	Initial Amount	Final Amount	Due Date	Analytical TAT	Dlv Rank	Comments	Output Sample Lab ID
1	MB~500-885/1 N/A	N/A		50 mL	50 mL	N/A	N/A	N/A		*MB~500-885/1-A*
2	LCS~500-885/2 N/A	N/A		50 mL	50 mL	N/A	N/A	N/A		*LCS~500-885/2-A*
3	500-119-A-11 (6010B)	N/A	Water	50 mL	50 mL	3/20/06	5_Days - R	5		*500-119-A-11-A*
4	500-119-A-11~DU (6010B)	N/A	Water	50 mL	50 mL	3/20/06	5_Days - R	5		*500-119-A-11-B~DU*
5	500-119-A-11~MS (6010B)	N/A	Water	50 mL	50 mL	3/20/06	5_Days - R	5		*500-119-A-11-C~MS*
6	500-119-A-11~MSD (6010B)	N/A	Water	50 mL	50 mL	3/20/06	5_Days - R	5		*500-119-A-11-D~MSD*
7	500-119-A-12 (6010B)	N/A	Water	50 mL	50 mL	3/20/06	5_Days - R	5		*500-119-A-12-A*
8	500-119-A-16 (6010B)	N/A	Water	50 mL	50 mL	3/20/06	5_Days - R	5		*500-119-A-16-A*
9	500-119-A-17 (6010B)	N/A	Water	50 mL	50 mL	3/20/06	5_Days - R	5		*500-119-A-17-A*

Metals/Inorganics Analysis Sheet

(To Accompany Samples to Instruments)

Batch Number: 500-885 Analyst: Cann, Randall Batch Open: 3/15/2006 6:15:00PM

Method Code: 500-3010A-500 Batch End: 3/15/2006 6:15:00PM

Reagent Additions Worksheet

Lab ID	Reagent Code	Amount Added	Final Amount	By	Witness
LCS 500-885/2	M05JSPKIC_00001	0.5 mL	50 mL		
500-119-A-11 MS	M05JSPKIC_00001	0.5 mL	50 mL		
500-119-A-11 MSD	M05JSPKIC_00001	0.5 mL	50 mL		

Other Reagents:

Reagent	Amount/Units	Lot#:

Metals/Inorgar Analysis Sheet

(To Accompany Samples to Instruments)

Batch Number: 500-893 Analyst: Cann, Randall Batch Open: 3/15/2006 7:30:00PM

Method Code: 500-3050B-500 Batch End:

Acid Digestion of Sediments, Sludges, and Soils

	Input Sample Lab ID (Analytical Method)	SDG	Matrix	Initial Amount	Final Amount	Due Date	Analytical TAT	Dlv Rank	Comments	Output Sample Lab ID
1	MB~500-893/1 N/A	N/A		1.0000 g	100 mL	N/A	N/A	N/A		*MB~500-893/1-A*
2	LCS~500-893/2 N/A	N/A		1.0000 g	100 mL	N/A	N/A	N/A		*LCS~500-893/2-A*
3	500-115-C-1 (6010B)	N/A	Solid	1.0194 g	100 mL	3/24/06	14_Days - R	2		*500-115-C-1-B*
4	500-115-B-2 (6010B)	N/A	Solid	1.0450 g	100 mL	3/24/06	14_Days - R	2		*500-115-B-2-B*
5	500-115-B-3 (6010B)	N/A	Solid	1.0066 g	100 mL	3/24/06	14_Days - R	2		*500-115-B-3-B*
6	500-115-B-4 (6010B)	N/A	Solid	1.0376 g	100 mL	3/24/06	14_Days - R	2		*500-115-B-4-B*
7	500-115-B-5 (6010B)	N/A	Solid	1.0613 g	100 mL	3/24/06	14_Days - R	2		*500-115-B-5-B*

Metals/Inorganics Analysis Sheet

(To Accompany Samples to Instruments)

Batch Number: 500-893 Analyst: Cann, Randall Batch Open: 3/15/2006 7:30:00PM

Method Code: 500-3050B-500 Batch End:

Reagent Additions Worksheet

Lab ID	Reagent Code	Amount Added	Final Amount	By	Witness
LCS 500-893/2	M05JSPKIC_00001	1 mL	100 mL		

Other Reagents:

Reagent	Amount/Units	Lot#:

SOP No.	Revision No.	Date	Page
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TITLE: Sample Preparation Semivolatile and Nonvolatile Organic Compounds from a WasteWater or Leachate Matrix using Separatory Funnel Extraction

Updated by:	Signature:	Date
Daniel A. Knieriemen Supervisor, Organic Extractions		07/19/06

Approved by:	Signature:	Date
Daniel A. Knieriemen Supervisor, Organic Extractions		07/19/06
David W. Mazur Env. Health & Safety Coor.		7/19/06
Terese A. Preston Quality Manager	Terese A. Preston	7/19/06

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1.0 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) outlines the extraction procedure of semivolatile and nonvolatile organic compounds from wastewater or leachate matrices using SW-846, Third Edition, Methods 1311, 3500B, and 3510C; and 40CFR, Part 136, Methods 608, 610, and 625 as references.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

Not Applicable - refer to the analytical SOPs.

1.1.2 Reporting Limits

Not Applicable - refer to the analytical SOPs.

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.2 Summary of Method

The following procedure is used for the separatory funnel extraction of semivolatile and nonvolatile organics from waste water and leachate matrices for subsequent analysis.

A measured volume of sample (usually 1-liter for waste waters and 100 mLs for leachates) at the appropriate pH is serially extracted with Dichloromethane (DCM, a.k.a., Methylene chloride) using the separatory funnel extraction procedure. The extract is dried, concentrated, exchanged to another solvent if necessary, adjusted to the appropriate final volume, and stored at 4 ± 2°C prior to analysis. Optional cleanup procedures may be performed upon request. The mandatory acid cleanup for PCB samples is described within this SOP. GPC, Florisil, sulfur removal cleanups, and silica gel cleanup are described in USP-003.

2.0 INTERFERENCES

- Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.
- Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic material.
- Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem.
- Matrix interferences may be caused by contaminants that are co-extracted from the sample. These can appear as large, distinct peaks and/or elevated baselines. Occasionally matrix interferences may prevent the proper detection of surrogate and/or analytes, resulting in the reporting of low, or possibly high, surrogate and/or spike recoveries. The extent of matrix interferences will vary considerably from sample to sample, depending upon the nature of the site being sampled. Various cleanup procedures may be performed to remove heavy background or interferences, including GPC cleanup, florisil cleanup, acid cleanup, silica gel cleanup, and sulfur removal procedures.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, the facility addendum to the CSM, and this document.

3.1 Specific Safety Concerns or Requirements

- The following analytes have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, PCBs, 3,3'dichlorobenzindine, benzo(a)pyrene, alpha-BHC, beta-BHC, gamma-BHC, delta-BHC, 4,4'-DDT, dibenz(a,h)anthracene and N-nitrosodimethylamine. Primary standards of these toxic compounds should be prepared in hood.
- The use of separatory funnels to extract aqueous samples with Methylene Chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and a face shield must be worn over safety glasses or goggle when it is performed.
- Nitrile or equivalent gloves are available and must be worn when handling acids, bases, or samples.
- All extractions and handling of solvents should be performed under well-ventilated conditions of a fume hood.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Acetonitrile	Flammable Poison	40 ppm-TWA	Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Sulfuric Acid	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.

1 – Always add acid to water to prevent violent reactions.
2 – Exposure limit refers to the OSHA regulatory exposure limit.

There are no materials used in this method that have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

4.0 EQUIPMENT AND SUPPLIES

4.1 Glassware

- 2 Liter separatory funnels
- 250 mL, 500 mL Erlenmeyer flasks
- Long stem glass funnels
- 100 mL, 1,000 mL graduated cylinder
- 500 mL Kuderna-Danish Flask
- 10 mL graduated receivers with attachments, regular and insulated types
- 3-Ball Snyder column
- 1.0 mL, 10.0 mL, class A, volumetric pipet
- 2.0 mL disposable pipet
- 500 uL, 1,000 uL syringe
- 5.0 mL, 10.0 mL pre-marked 16 X 125 test tubes with Teflon lined lids*
- Glass stirring rods
- Shallow Pyrex drying tray
- Teflon squeeze bottles
- Teflon centrifuge bottles, 125 mL

*Volumetrically add the appropriate volume of Hexane to a 16 X 125 screw top test tube and mark the meniscus using a fine-tipped marker. Discard the Hexane into an appropriate waste vessel and let dry. Dilute the sample to volume using this test tube.

4.2 Miscellaneous

- glasswool, soxhlet-extracted using DCM
- transfer pipets
- wide range pH paper 1 to 12
- Centrifuge
- Boiling Chips, Teflon, soxhlet-extracted using DCM
- Muffle furnace
- Desiccator
- Balance, top-loading, capable of weighing to 0.001g
- Waterbath, heated, with concentric ring covers, capable of temperature control - Must be in a hood
- Nitrogen Evaporator - N-Evap by Organomation Associates, Inc.

5.0 REAGENTS AND STANDARDS

A label on any reagent or standard bottle must contain the standard number, concentration of the reagent, name of the reagent, date prepared, expiration date and the analyst who prepared the reagent.

5.1 Reagents

5.1.1 Pesticide Grade Methylene Chloride [Dichloromethane (DCM)]
Pesticide Grade Acetone
Pesticide Grade Hexane
Pesticide Grade Acetonitrile

5.1.2 Heat Purified Granular Sodium Sulfate

Purify by heating to 400°C for 4-hours in a shallow drying tray, cool in a desiccator, and store in a glass bottle.

- Life of Reagent: 1-year
- Storage Requirements: Store in a glass container and keep dry (anhydrous).

5.1.3 Reagent Water

Defined as water in which no interferent is observed at one-half the reporting limit of any target compounds when one liter of the reagent water is extracted and prepared by using the same procedure as for a water sample.

5.1.4 Concentrated Sulfuric Acid

Purchased from a supplier

- Hazardous Properties: Sulfuric Acid (H_2SO_4) is extremely corrosive and toxic to tissues. Vapors are also harmful.
- Life of Reagent: 1-year
- Storage Requirements: Store in glass container. The label on the bottle must contain concentration and name of reagent.

5.1.5 Sulfuric Acid (1:1)

Cautiously add 500 mLs concentrated sulfuric acid to 500 mLs reagent water. Because this is an exothermic reaction, prepare in Pyrex glassware and in a cold water bath.

- Hazardous Properties: Extremely corrosive and toxic to tissues. Vapors are also harmful.
- Life of Reagent: 1-year from preparation date
- Storage Requirements: Store in a glass bottle

5.1.6 10 N Sodium Hydroxide

Cautiously dissolve 200 grams of solid NaOH in reagent water and dilute to 500 mLs. Always prepare in Pyrex glassware due to the amount of heat given off by the reaction.

- Hazardous Properties: Toxic & Corrosive. Harmful if swallowed, inhaled or absorbed through the skin.
- Life of Reagent: 1-year from preparation date
- Storage Requirements: Store in a glass bottle.

5.2 Quality Control (QC) Solutions

QC solutions must be stored in amber or foil-wrapped, glass containers that have Teflon-lined caps. The label on the container must contain the following information: Name of the solution, the standard number, concentration of the components, date prepared, preparation analyst, and expiration date. All QC solutions are stored in the standards refrigerator in the GC/MS lab, GC Extractables lab, or in the standards refrigerator located in the organic extraction lab. QC solutions are stored at $4 \pm 2°C$.

Listed below are the various QC solutions and concentrations appropriate for extraction of BNAs, Pesticides, Pesticides/PCBs, PCBs, PAHs, and diesel range organics (DRO) from waste water and TCLP Leachate samples.

5.2.1 Surrogate Spike Solutions

5.2.1.1 BNA Surrogate Spike Solution

The BNA Surrogate Spike Solution is purchased directly from a chemical vendor at the levels listed below. 500 uLs of BNA Surrogate Spike Solution is added to all samples, the method blank (MB), matrix spike/matrix spike duplicate (MS/MSD) and laboratory control sample (LCS).

Compound	Concentration (ug/mL)
p-Terphenyl-d_4	100
Nitrobenzene-d_5	100
2-Fluorobiphenyl	100
1,2-Dichlorobenzene-d_4	100
Phenol-d_5	150
2-Fluorophenol	150
2,4,6-Tribromophenol	150
2-Chlorophenol-d_4	150

- Life of Standard: 6 months from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2

5.2.1.2 BNA Surrogate (SIM) Spike Solution

The BNA Surrogate (SIM) Spike Solution is prepared from the BNA Surrogate Spike Solution. 500 uLs of BNA Surrogate Spike Solution is added to all samples, the MB, MS/MSD and LCS.

Compound	Concentration (ug/mL)
p-Terphenyl-d_4	10
Nitrobenzene-d_5	10
2-Fluorobiphenyl	10
1,2-Dichlorobenzene-d_4	10
Phenol-d_5	15
2-Fluorophenol	15
2,4,6-Tribromophenol	15
2-Chlorophenol-d_4	15

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2

5.2.1.3 BNA Surrogate Spike (Low –Level 'L' Matrix)Solution

The BNA Surrogate Spike ('L' Matrix) Solution is prepared from the BNA Surrogate Spike Solution. 500 uLs of BNA Surrogate Spike Solution is added to all samples, the MB, MS/MSD and LCS.

Compound	Concentration (ug/mL)
p-Terphenyl-d_4	50
Nitrobenzene-d_5	50
2-Fluorobiphenyl	50
1,2-Dichlorobenzene-d_4	50
Phenol-d_5	75
2-Fluorophenol	75
2,4,6-Tribromophenol	75
2-Chlorophenol-d_4	75

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2

5.2.1.4 Pesticide/PCB Surrogate Spike Parent Solution

A certified stock solution is purchased directly from a standards vendor. The GC Extractables lab prepares a surrogate parent solution from these standards and is a solution of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TCX) in acetone at the concentrations listed below. Refer to the analytical SOP for specific details on the preparation, storage and labeling of these solutions. The parent surrogate is also used in the extraction of pesticides from TCLP leachates. 1,000 uLs of Pesticide/PCB Surrogate Spike Solution is added to all samples, the MB, MS/MSD and LCS.

Compound	Concentration (ug/mL)
DCB	4.0
TCX	4.0

- Life of Standard: 6 months from date of preparation, not to exceed expiration date of standards
- Storage Requirements: As stated in Section 5.2

5.2.1.5 Pesticide/PCB Surrogate Spike Solution

The surrogate used in the extraction of pesticides/PCBs from waste waters is a solution of DCB and TCX in acetone at the concentrations listed below. The working solution is prepared from the parent solution by performing a 1/10 dilution using Class A volumetric glassware in acetone. 1,000 uLs of Pesticide/PCB Surrogate Spike Solution is added to all samples, the MB, MS/MSD and LCS.

Compound	Concentration (ug/mL)
DCB	0.40
TCX	0.40

- Life of Standard: 6 months from date of preparation, not to exceed expiration date of the parent standard
- Storage Requirements: As stated in Section 5.2

5.2.1.6 PAH Surrogate Spike Solution

The surrogate used in the extraction of PAHs from soil/sediments is a solution of Decafluorobiphenyl and Benzo (e) pyrene in acetone at the concentrations listed below. The HPLC group prepares the working surrogate solution. 500 uLs of PAH Surrogate Spike Solution is added to all samples, the MB, MS/MSD and LCS.

Compound	Concentration (ug/mL)
Decafluorobiphenyl	100
Benzo (e) pyrene	5.0

- Life of Standard: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.1.7 DRO Surrogate Spike Solution

The surrogate used in the extraction of DRO from soil/sediments is a solution of 2-Fluorobiphenyl and o-Terphenyl in acetone at the concentrations listed below. The GC group prepares the working surrogate solution. 500 uLs of DRO Surrogate Spike Solution is added to all samples, the MB, MS/MSD and LCS.

Compound	Concentration (ug/mL)
2-Fluorobiphenyl	200
o-Terphenyl	200

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

5.2.2 Laboratory Control Sample (LCS) & Matrix Spike (MS) Solutions

5.2.2.1 BNA TCL Spike Solution

The BNA TCL Spike Solution is purchased directly from vendor at the levels listed below. 1000 uLs of BNA TCL Spike Solution is added to the MS/MSD and LCS.

Compound	Concentration (ug/mL)
Acid Compounds	100
Base/Neutral Compounds	100

- Life of Standard: 6 months from the from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2.

5.2.2.2 BNA Matrix Spike (SIM) Solution

The BNA Matrix Spike (SIM) Solution is prepared from the BNA TCL Spike Solution found in section 5.2.2.1. 1000 uLs of BNA Matrix Spike (SIM) Solution is added to the MS/MSD and LCS.

Compound	Concentration (ug/mL)
Acid Compounds	10
Base/Neutral Compounds	10

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

5.2.2.3 BNA Matrix Spike (Low Level 'L' Matrix) Solution

The BNA Matrix Spike ('L' Matrix) Solution is prepared from the BNA TCL Spike Solution found in section 5.2.2.1. 1000 uLs of BNA Matrix Spike ('L' Matrix) Solution is added to the MS/MSD and LCS.

Compound	Concentration (ug/mL)
Acid Compounds	50
Base/Neutral Compounds	50

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

5.2.2.4 Pesticide (Full List) Spike Solution

The LCS/MS solution used in the extraction of pesticides or pesticides/PCB from soil/sediments is a solution of pesticide compounds in methanol at the following concentrations. 1000 uLs of Pesticide (Full List) Spike Solution is added to MS/MSD and LCS.

Compound	Concentration (ug/mL)
All compounds	0.40

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

5.2.2.5 PCB Spike Solution

The LCS / MS spike solution used in the extraction of PCBs from waste waters is a solution of Arochlor 1016 and Arochlor 1260 in methanol at the following concentrations. 1,000 uLs of PCB Spike Solution is added to the MS/MSD and LCS.

Compound	Concentration (ug/mL)
AR1016	5.0
AR1260	5.0

- Life of Standard: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.2.6 TCLP Pesticide Spike Solution

The LCS / MS spike solution used in the extraction of pesticides from TCLP leachates is a solution of pesticide compounds in methanol at the following concentrations. 1,000 uLs of TCLP Pesticide Spike Solution is added to the MS and LCSs that are for Pesticides only

Compound	Concentration (ug/mL)
Lindane	1.0
Heptachlor	1.0
Heptachlor Epoxide	1.0
gamma-Chlordane	1.0
Endrin	1.0
Methoxychlor	10.0

- Life of Standard: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.2.7 Toxaphene Spike Solution

The LCS / MS spike solution used in the extraction of pesticides from TCLP leachates is a solution of toxaphene in methanol at the following concentration. 1,000 uLs of Toxaphene Spike Solution is added to the LCS and MSs that are for PCBs only.

Compound	Concentration (ug/mL)
Toxaphene	100

- Life of Standard: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.2.8 PAH Spike Solution

The LCS/MS solution used in the extraction of PAHs from soil/sediments is a solution of analytes in acetonitrile at the following concentrations. The HPLC group prepares the spike solution. 500 uLs of PAH Spike Solution is added to the MS/MSD and LCS.

Compound	Concentration (ug/mL)
Acenaphthene	8
Acenaphthylene	16
Anthracene	0.8
Benzo(a)anthracene	0.8
Benzo(a)pyrene	0.8
Benzo(b)fluoranthene	1.6
Benzo(ghi)perylene	1.6
Benzo(k)fluoranthene	0.8
Chrysene	0.8
Dibenzo(a,h)anthracene	1.6
Fluoranthene	1.6
Fluorene	0.8
Indeno(1,2,3-cd)pyrene	0.8
Naphthalene	8.0
Phenanthrene	0.8
Pyrene	0.8

- Life of Standard: Same as the parent solution.
- Storage Requirements: As stated in Section 5.2.

5.2.2.9 DRO Spike Solution

The LCS/MS solution used in the extraction of DRO from soil/sediments is a solution Diesel Fuel #2 at 1000 ug/mL in methanol. The GC group prepares the spike solution. 500 uLs of DRO Spike Solution is added to the MS/MSD and LCS.

Compound	Concentration (ug/mL)
Diesel Fuel #2	4,000

- Life of Standard: Same as the parent solution.
- Storage Requirements: As stated in Section 5.2.

6.0 CALIBRATION

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

The following QC is performed with each organic extraction batch. An extraction batch contains samples of similar matrix that are logged in for the same test code. An extraction batch may contain no more than 20 samples.

Quality Control	Frequency
MB	1 in 20 or fewer samples
LCS [1]	1 set of 20 or fewer samples
MS/MSD [2]	At least one set in 20 or fewer samples (may be requested by client)
Surrogates	Every sample / MB / MS / MSD / LCS

[1] LCS Duplicate (LCSD) is performed when insufficient sample is available for the MS/MSD or if requested by the client.
[2] The sample selection for MS/MSD is rotated among client samples so that various matrix problems may be noted and/or addressed.

7.2 Sample Collection, Preservation and Handling

Sample container, preservation technique and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract/client requests. In general, water samples are collected in 1-liter or 80-oz. narrow-mouth, amber, glass jars, with Teflon-lined screw-cap lids. If a Teflon-lined lid is not available, solvent-rinsed aluminum foil can be used as a liner.

NOTE: If the sample matrix is highly acidic or basic, corrosion of the foil may occur and contaminate the sample.

Matrix	Holding Time (VTS) [1]	Preservation
Wastewaters	7 days	Cool, 4 ± 2°C
TCLP Leachates	14 days to TCLP Extract [2] 7 days from the completion of the TCLP extraction for the organic extraction	Cool, 4 ± 2°C

[1] Verified Time of Sampling.
[2] TCLP Extraction performed by Inorganic Prep Group.

Samples, sample extracts and standards are stored separately. Samples are stored at 4 ± 2°C prior to extraction. Any samples received by the preparation group that do not comply must be noted. Deviations in results "could" be explained by the failure of sample collector/client/custodian to comply to sample collection and storage requirements.

7.3 Sample Preparation (Glassware Preparation)

7.3.1 All glassware (except Snyder columns, volumetric flasks, volumetric pipets, and syringes) must be washed thoroughly with warm soapy water, rinsed **5** times with hot tap water and rinsed **3** times with DI water. The stopcocks of the separatory funnels should be cleaned with a small brush. **It is absolutely mandatory that all glassware be scrupulously clean.** Failure to rinse well with water, may leave a soap film that is incompletely removed with solvent rinsing, and with subsequent extraction, "soap" peaks will appear in the chromatograms.

7.3.2 If glassware is very wet it may be towel dried. **All** Glassware should be rinsed with cleaning grade acetone, and the excess should be discarded into the appropriate waste container. This step is performed to ensure that the glassware is dry. **If after rinsing once, the glassware still contains any water, repeat the acetone rinse.** At this point let the glassware dry before continuing to ensure that all of the water is gone. All glassware should then be rinsed with DCM using a Teflon squeeze bottle, and the excess discarded into the appropriate waste container. Repeat this step at least 3-times and allow the glassware to dry. Failure to remove all water prior to DCM rinsing prevents the DCM solvent from coming into contact with all surfaces on the glassware. The solvent rinse is then incomplete, and may leave contaminants on the glass, which are then co-extracted with the sample.

NOTE: DCM is considered a health hazard. It is harmful if swallowed or inhaled. The vapor is irritating and thus should be used in a hood. It is readily absorbed through the skin and contact may be irritating.

NOTE: Pressure builds up quickly in a capped separatory funnel. Vent the pressure immediately and often thereafter.

7.3.3 Procedures for Return of Glassware to Dishroom

Any glassware that has organic residue present, all K-D receivers, and all separatory funnels should be rinsed with cleaning grade acetone, or whatever other solvent which removes the residue, prior to return to the dish room from the lab. Glassware in which the residue can not be removed should be segregated from other glassware being returned to the dish room. Glassware should be carefully placed in a tub and placed on the "Dirty" side of the dish racks. In order to reduce glassware breakage, glassware should not be stacked in the tubs. Severely chipped glassware should be removed from service. Some items are repairable. Check with the supervisor as to what items get repaired.

7.4 Calibration/Standardization

Not Applicable.

7.5 Preventive Maintenance

- Balance should be cleaned and checked for levelness prior to each use. Class "S" weights should be weighed and documented each day the balance is used. Consult your supervisor if the weights are out of acceptable limits. Do not use the balance until the situation is back in control.
- The K-D water bath should contain DI water only. The water level should be checked prior to each use, and should not fall below the heating coils. If the heating coils do become exposed to the air while in use, they could burn-out and would require replacement. Keep the water level approximately one inch from the top of the bath edge.
- The N-Evap water bath should also contain DI water. The water level in the bath should be sufficient to cover 3/4 of the receivers when submerged.
- The thermometer used in the extraction water baths are checked against a reference NIST thermometer on a yearly basis or sooner if necessary.
- The desiccant used in the desiccator should be removed and dried in an oven at 130°C whenever the color indicates that it is saturated with moisture. This is usually indicated by a change of color from blue to purple/pink.
- To avoid the breakage of sample extracts, the analyst needs to take care that the containers are properly balanced on the centrifuge. The container should fit snugly in the holder. Use a paper towel to cushion the centrifuge bottles if necessary.

7.6 Extraction Process

7.6.1 MB and LCS Water Preparation

Add 1.0 liter of Milli-Q water to 2 separatory funnels and label as the MB and LCS.

BNA TCLP Add 1.0 L of Milli-Q water to a separatory funnel and label as the LCS.

7.6.2 Sample Preparation

Prior to pouring water samples, sample containers should be inverted a few times to mix the sample. However, if there is a sediment layer present, consult your supervisor or section manager before mixing. Also, if the sample appears to have more than one phase, immediately contact your supervisor, section manager, or project manager. The client will need to be notified.

a. Waste Waters

If the sample container is 1-liter or 1-quart in volume, mark the level on the outside of the bottle. Pour the entire contents of the bottle into the separatory funnel. Rinse the bottle with 60 mls of DCM (the first aliquot of the extraction, and add it to the extraction vessel. This ensures that the sample is qualitatively transferred. Refill the bottle to the mark with water and then measure the volume in the bottle. Record this amount as the initial sample volume. Occasionally the analyst will encounter samples that contain sediment which has collected at the bottom of the sample bottle. The bottle still must be rinsed with DCM and the DCM/sediment transferred to the separatory funnel. If emulsion occurs, the DCM can be separated by using the centrifuge (see **7.6.9.2 Centrifugation**). If a sample contains an unreasonable amount of sediment (1/4 inch or more) contact the supervisor before continuing. Alternatively, a graduated cylinder for each sample can be used to determine initial sample volume. If a graduated cylinder is used, both it and the sample bottle must be rinsed with the first aliquot of DCM.

Use 1.0 liter aliquots for MS/MSD if sample volume allows. Label as the sample, MS and MSD.

b. TCLP Leachates

Measure 900 mLs of Milli-Q water into each sample separatory funnel. Measure 100 mLs of each sample and add it to the labeled separatory funnel containing the water.

BNA & Pesticide TCLP Measure an additional 100 mL aliquot of those samples designated to have a MS. LCSD and MSD are not performed.

7.6.3 Check the pH by dipping a transfer pipet into the sample and touching it to wide-range pH paper. Record the pH in the extraction log.

7.6.4 Add the appropriate amount of the appropriate surrogate spike solution to every sample including the MB, MS/MSD and LCS.

7.6.5 Add the appropriate amount of the appropriate spike solution to the LCSs and MSs.

NOTE: All spiking solutions MUST be at room temperature before use. This includes stock solutions when preparing working spike solutions. Actual concentrations will change at colder temperatures. Furthermore, some components may come out of solution in the freezer. Warming to room temperature reverses the process.

7.6.6 Adjust the pH as required (refer to Chart in Attachment 1 for the appropriate pH for each parameter). Use sulfuric acid (1:1) to acidify and NaOH (10N) to make basic. Record pH adjustments in the log book.

7.6.7 Plug a long-stem glass funnel with a little soxhlet-extracted glass wool. Fill the funnel half-full with heat-purified granular sodium sulfate and place on a 250 mL collecting flask (500 mLs for BNA). Be sure each separatory funnel and corresponding collecting flask is appropriately labeled with the correct sample number, extraction batch number, and method code.

7.6.8 Seal and shake the separatory funnel vigorously for 2-minutes with periodic venting to release excess pressure.

CAUTION: Pressure builds up quickly in a separatory funnel that has both the stopcock closed and the stopper in place. Initial venting should be done immediately after the separatory funnel has been sealed and inverted. Be sure to vent the separatory funnel frequently by inverting the funnel and opening the stopcock. Do not point the funnel at or near anyone as it is being vented.

7.6.9 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ one or more of the following techniques to complete the phase separation (document the presence of severe emulsions in the log book).

7.6.9.1 Stirring Rod

Physically break up the emulsion by stirring.

7.6.9.2 Centrifugation

Separates by density. Draw off the emulsion into a 125 mL, Teflon, centrifuge bottle. Balance the centrifuge. Centrifuge 2-5 minutes. Carefully pour the contents back into the separatory funnel and drain off the DCM layer. Alternatively, after centrifugation, draw out the DCM (bottom layer) directly from the centrifuge bottle using a disposable, 10 mL pipet and deliver it to the collecting flask. Return any aqueous phase back to the appropriate separatory funnel. Add the next DCM aliquot first to the centrifuge bottle as a rinse and then to the appropriate separatory funnel.

7.6.9.3 Salting Out

Addition of salt makes the aqueous phase too polar to support a less polar phase. Add ~100 to 200 g of heat-purified sodium chloride to the aqueous phase and shake the sample again.

7.6.10 Drain the organic layer through the funnel containing sodium sulfate and into the 250 mL collecting flask.

7.6.11 Repeat the extraction 2 more times using 60 mLs of DCM each time, combining all 3 organic layers in the same flask. Rinse down the sodium sulfate with ~20 mLs of DCM after the first and last drain. Unless BNA, the sample is now ready for concentration. Proceed to Section 7.6.12 for K-D concentration instructions

BNA Samples The samples are adjusted to pH>11 and extracted 3-more times as described above, after which, the samples are ready for concentration. Proceed to Section 7.6.12 for K-D concentration instructions.

7.6.12 Sample Concentration

Occasionally, samples extracted from wastewaters for subsequent BNA analysis and/or Pesticide/PCB analysis receive a gel permeation cleanup (GPC). These samples need to be identified prior to concentrating. Refer to the appropriate section of USP-001 or 003 for the concentration of these "pre-GPC" BNA samples. Refer to the appropriate section of USP-003 for the concentration of these "pre-GPC" Pesticide/PCB samples.

7.6.12.1 Assemble a K-D concentrator by attaching a 10 mL concentrator tube (insulated type if BNA or DRO) to a 500 mL K-D flask. Add a couple of boiling chips. Transfer each extract to its own K-D flask (making sure that each flask is appropriately labeled). Rinse the Erlenmeyer flask 3 times with DCM, adding each rinse to the K-D flask. Rinse down the joint with DCM and then attach a 3-ball Snyder column to each and place on the water bath. The temperature control should be set at medium. This setting should correspond to 80-90°C. Concentration to <10 mLs is usually completed in 60-90 minutes. The balls should chatter but the chambers should not flood.

7.6.12.2 Refer to appropriate test for further concentration instructions.

BNA and DRO When the apparent final volume reaches about 2-5 mLs, remove from the bath. Allow to drain and cool for 10 minutes. Remove the Snyder column, rinsing the joint and flask with 1-2 mLs DCM. Allow to drain. Dry off the outside of the joint between the flask and receiver to remove the water. Pull the 2 pieces apart gently, in a twisting motion. Rinse off the joint with DCM into the receiver. Cover the receiver with a piece of aluminum foil. If the extracts are to sit overnight, they are to stored at 4 ± 2°C.

Proceed to Section 7.6.13 for further concentration using nitrogen evaporation.

PCB and Pesticide/PCB When the apparent volume reaches ~ 5 mLs, a solvent exchange is required. Add 50 mLs of hexane to the K-D flask (through the Snyder column). Concentrate the extract by raising the temperature of the water bath, if necessary, to maintain proper distillation. The Snyder column may be wrapped with aluminum foil to aid in proper evaporation. When the apparent volume reaches 3-5 mLs, remove from the bath. Allow to drain and cool for 10 minutes. Remove the Snyder column, rinsing the joint and flask with 1-2 mLs hexane. Allow to drain. Dry off the outside of the joint between the flask and receiver to remove the water. Pull the 2 pieces apart gently, in a twisting motion. Rinse off the joint with hexane into the receiver.

Transfer the extract into a labeled, 16X125 test tube that has been previously marked at 10.0 mLs. Rinse the receiver 3 times with hexane, transferring the rinsate each time to the 16X125 test tube. Refrigerate the extracts if they are not going to be immediately concentrated.

Proceed to Section 7.6.13 for further concentration using nitrogen evaporation.

PAHs When the apparent volume reaches ~5 mLs, a solvent exchange is required. Add 5 mLs of acetonitrile to the K-D flask (through the Snyder column). Concentrate the extract by raising the temperature of the water bath, if necessary, to maintain proper distillation. The Snyder column may be wrapped with aluminum foil to aid in proper evaporation. When the apparent volume reaches 3-5 mLs, remove from the bath. Allow to drain and cool for 10 minutes. Remove the Snyder column, rinsing the joint and flask with 1-2 mLs acetonitrile. Allow to drain. Dry off the outside of the joint between the flask and receiver to remove the water. Pull the 2 pieces apart gently, in a twisting motion. Rinse off the joint with acetonitrile into the receiver.

Transfer the extract into a labeled, 16X125 test tube that has been previously marked at 5.0 mLs. Rinse the receiver 3 times with acetonitrile, transferring the rinsate each time to the 16X125 test tube. Refrigerate the extracts if they are not going to be immediately concentrated.

Proceed to Section 7.6.13 for further concentration using nitrogen evaporation.

7.6.13 Nitrogen Evaporation

7.6.13.1 For further concentration, place each receiver or test tube on the N-Evap tray. The N-Evap outlet needles should be stored in a 600 mL beaker containing DCM:Acetone (1:1) mixture prior to each use. Wipe each outlet needle with a KimWipe and lock into place on the N-Evap. Lower the outlet tube into the receiver being careful not to touch the sides of the receiver. The outlet tube should remain above the surface of the extract. Open the valve of the nitrogen tank and adjust the pressure in order to achieve the appropriate nitrogen stream. The nitrogen stream should make a slight "dimple" in the surface of the extract. If the extract bubbles, the nitrogen stream is **not** gentle enough. Lower the entire N-Evap tray into the warm water bath to aid the

evaporation process. Heat is not necessary and if used the temperature should not exceed 35°C.

7.6.13.2 The extracts must never be allowed to go dry. While the extracts are concentrating, occasionally rinse down the sides of the receiver or test tube with appropriate solvent (see corresponding test instructions below).

7.6.13.3 Refer to appropriate test below for further concentration instructions.

BNAs

7.6.13.5a Once the extracts reach ~0.5 mLs, remove from the N-Evap. Label a 1.5-2 mL screw capped vial with appropriate sample number and batch number. Transfer the 0.5 mLs to the vial using a transfer pipet. Rinse the receiver well with a little (<1/4 mL) DCM and add to the vial. Compare the sample volume in the vial to a pre-marked, 0.9 mL vial. Rinse receiver with a little more DCM (<1/4 mL). Transfer to sample vial. Compare the volume to the pre-marked 0.9 mL vial. Dilute the sample (if necessary) to 0.9 mLs with another DCM rinsate. The extraction analyst must rinse the receiver at least 2-times and stay at or below 0.9 mLs. The use of a 500 uL syringe gives the analyst more control when adding the small-volume DCM rinses to the receiver. If the rinsates make the extract more than the 0.9 mL, the analyst may hold the vial under the stream of nitrogen momentarily to reduce the volume back down to 0.9 mL. The GC/MS analyst will bring the sample extract to exactly 1.0 mL prior to analysis. Seal vial with a Teflon-lined screw-cap.

There will be samples that will not concentrate to a 1 mL final volume. In these cases, bring the sample up to the smallest final volume (increments of 1 mL)* that the sample and 3 rinses will transfer into. All changes in final volume must be documented in the extraction logbook. Notify your supervisor.

* Volumetrically add the appropriate volume of DCM to a 16 X 125 screw top test tube and mark the meniscus using a fine-tipped marker. Discard the DCM into an appropriate waste vessel. Bring up sample to volume using this test tube.

7.6.13.6a All samples pertaining to one extraction batch are placed in a plastic vial holder and secured. A listing of the entire contents of the batch, including clients, sample numbers, batch number, standard numbers, and date extracted, is to be placed WITH the set. To relinquish samples, the extraction analyst takes the sample extracts and the extraction logbook to the sample extract refrigerator (located in the GC/MS Lab).

7.6.13.7a An analyst from the GC/MS BNA group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction logbook. All extracts are to be kept at 4 ± 2°C in the dark, until analysis.

PCBs and Pesticide/PCB

7.6.13.4b Concentrate the sample to 2-3 mLs and dilute to the 10.0 mL mark with hexane.

PCBs Refer to mandatory sulfur acid cleanup (Sec. 7.6.16)

TCLP The final volume is 100 mL, however, the GC/Extractables Group does the 1/10 dilution prior to analyzing.

7.6.13.5b All samples pertaining to one extraction batch are placed in a test tube rack. Each test tube should have the extraction batch number, sample #, and test code written on it.

7.6.13.6b To relinquish samples, the extraction analyst takes the sample extracts and the extraction logbook to the sample cooler area (located in the GC Extractables Lab). An analyst from the GC Extractables group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction log book. All extracts are to be kept at 4 $\pm$ 2°C in the dark, until analysis.

PAHs

7.6.13.4c Concentrate the sample to ~2 mLs to remove any remaining DCM. Dilute the sample up to 5.0 mLs with acetonitrile.

7.6.13.5c All samples pertaining to one extraction batch are placed in a test tube rack. Each test tube should have the extraction batch number, sample #, and test code written on it.

7.6.13.6c To relinquish samples, the extraction analyst takes the sample extracts and the extraction logbook to the sample cooler area (located in the GC Extractables Lab). An analyst from the HPLC group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction logbook. All extracts are to be kept at 4 $\pm$ 2°C in the dark, until analysis.

Diesel/DRO

7.6.13.4d Concentrate the sample to the 5.0 mL mark. If the solvent goes below the 5.0 mL mark, dilute to 5.0 mLs with DCM.

7.6.13.5d All samples pertaining to one extraction batch are placed in a test tube rack. Each test tube should have the extraction batch number, sample #, and test code written on it.

7.6.13.6d To relinquish samples, the extraction analyst takes the sample extracts and the extraction logbook to the sample cooler area (located in the GC Extractables lab). An analyst from the GC Extractables group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction log book. All extracts are to be kept at 4 ± 2°C in the dark, until analysis.

7.6.14 Screening and Cleanup

7.6.14.1 Samples are not pre-screened prior to extraction. Unless previous experience has proven high concentrations and/or background, a 1-liter sample will be extracted.

7.6.14.2 Sludge samples are a mixture of water and suspended solid materials. If the percent moisture of a given sludge is > 90%, a 10 g or 30 g portion may be weighed and added to 1-L of reagent water. It is then extracted like a water matrix as described in this procedure. Despite the extraction method, sludges are generally reported on a dry weight basis and the total solids result must be entered into the spreadsheet.

7.6.14.3 PAH samples do not receive any cleanup procedures.

7.6.15 Extract Cleanup by Gel Permeation Chromatography (GPC)

7.6.15.1 It is not mandatory that BNA or Pesticide/PCB samples be subjected to further cleanup steps prior to analysis. However, if it is requested that these sample sets receive a GPC cleanup, refer to the appropriate section of the USP-003.

7.6.15.2 It is not mandatory that Pesticide/PCB samples be subjected to further cleanup steps prior to analysis. However, if it is requested that the Pesticide/PCB set receives a Florisil cleanup, refer to the appropriate sections of USP-003.

7.6.15.3 It is not mandatory that DRO sample be subjected to further cleanup procedures prior to analysis. However, if it is requested that the DRO set receives a Silica Gel cleanup, refer to the appropriate section in USP-008.

7.6.16 Mandatory Acid Cleanup for PCBs

If the sample is to be analyzed for **PCBs ONLY**, a mandatory sulfuric acid cleanup is performed. Add ~3-4 mLs of concentrated H_2SO_4 to the extract (contained in a screw-top test tube). Shake vigorously for a least 1 minute. Centrifuge the hexane/acid for at least a couple minutes to ensure adequate separation. If the acid layer (the bottom layer) is dark in color, transfer the hexane layer (the top layer) to another screw-top test tube and repeat the acid cleanup. The acid cleanup should be repeated until the acid layer no longer turns dark in color. The hexane extract must always be immediately removed from the acid and transferred into another clean, labeled, screw-top test tube. Document acid cleanup in comment section of the extraction logbook. Relinquish the samples as described in the nitrogen evaporation section.

7.7 Documentation

7.7.1 All extraction information must be carefully documented in the appropriate extraction log (Attachment 2). Any additional sample or extraction information is recorded in the comment section of the extraction log. All problems and/or deviations from normal procedures must be documented in the extraction log. The supervisor should be notified and a Sample Discrepancy Report (SDR) may need to be initiated.

7.7.2 Different parameters are given different test methods within LIMS. Refer to the batch paperwork for the assigned test methods.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 Method Blank (MB)

The MB is reagent (Milli-Q) water, which has been spiked with the appropriate surrogate, then taken through the entire extraction procedure and is used to monitor the introduction of artifacts into the process. This demonstrates that the materials used are free of interferences.

8.1.2 Laboratory Control Sample (LCS)

The LCS is reagent (Milli-Q) water, which has been spiked with a predetermined quantity of spike solution with the appropriate analytes of interest and the appropriate surrogate.

8.1.3 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

In MS/MSD analysis, predetermined quantities of spike solutions of specified analytes and appropriate surrogate are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are

calculated for each of the analytes detected by the analysis. The relative percent difference between the samples is calculated and used to assess analytical precision.

8.1.4 Surrogate

A surrogate is an organic compound(s) which is similar to the analytes of interest in chemical composition, extraction and chromatography, but which is not normally found in environmental samples. The surrogate is added to **all** samples, MBs, MS/MSD and LCS prior to extraction and analysis. Percent recoveries are calculated for each surrogate.

8.1.5 Sometimes PCBs are extracted in the same extraction batch as Pesticide samples. When this occurs, the QC includes one MB; one LCS/LCSD for the pesticide compounds; one LCS/LCSD for PCB compounds; one MS/MSD for the pesticide compounds; and one MS/MSD for PCB compounds.

8.1.6 LCDs and MSDs are not performed for BNA TCLP.

8.1.7 LCSD and MSDs are not performed for Pesticide TCLP samples. However, an LCS/LCS along with a MS/MS are extracted and recorded. The TCLP Pesticide Spike and Toxaphene Spike need to remain separate from one another.

8.2 Corrective Action

The extraction analyst must perform the Quality Control described in Section 7.1. The extraction analyst will not know if all QC is in control until the GC/MS, GC/Extractables, or HPLC group analyzes the extracts and determine the results of the MBs, MS/MSDs, LCSs, and surrogate recoveries. It is the responsibility of the analysis group to inform the Organic Extractions Department by documenting in the "BNA Re-Extraction Log" or by initiating a Sample Discrepancy Report (SDR) when a sample or set of samples requires re-extraction. Re-extractions are to be designated as R1 in the extraction process.

All problems and/or deviations from normal procedures must be documented in the extraction logbook. Your supervisor should be notified and a SDR may need to be initiated.

9.0 DATA ANALYSIS AND CALCULATIONS

Not Applicable.

10.0 WASTE MANAGEMENT AND POLLUTION CONTROL

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Waste flammable solvents. Solvents will be collected in a waste jar and poured into the Waste Chlorinated Solvent drum using a funnel to reduce splashing.
- Extracted water samples will be poured into the Waste Water drum using a funnel to reduce splashing.
- Remaining solid waste produced by this method shall be disposed of into the Non-Hazardous Waste solids containers.
- Any unused extracts remaining from this method shall be turned over to the EHSC to be collected for disposal.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Section 1, 7 and 8.

12.0 REFERENCES

Refer to Sections 1, 6, 7 and 8.

13.0 ATTACHMENTS

Attachment 1. Example: Extraction Logbook / LIMS Batch Data
Attachment 2. Example: Procedural Flowcharts
Attachment 3: Example: BNA Surrogate Stock Solution
Attachment 4: Example: 8270 LCS Mix
Attachment 5: Example: 3,3'-Dimethylbenzidine
Appendix 1: BNA Halowax
Appendix 2: Alachlor/Atrazine
Appendix 3: Wisconsin DRO
Appendix 4: JP4/JP8

Historical File: Revision 00: 03/22/99
Revision 01: 03/14/00
Revision 02: 09/21/00
Revision 03: 05/19/04
Revision 04: 04/14/05
Revision 05: 07/18/06

Reasons for Change: Revision 05:

- Annual update
- Removal of all Organophosphorus Pesticide references
- Removal of LabNet, replaced with LIMS
- Edited section 7.6.2 for rinsing of sample bottles

U:QC\SOP\USP\USP-3510.DOC

Attachment 1.

Example: Extraction Logbook / LIMS Batch Data

Extraction Date:_____ STL Chicago Page No.:_____
Method Code:_____ Organic Extraction Record Batch No.:_____
Solvent:_____ GC/MS Semi-Volatiles Analyst Initials:_____
Solvent Lot No.:_____ Balance ID No.:_____
Solvent Dispenser Volume Checked:_____
Acid / Base (circle & define):_____ Lot No.:_____ Sodium Sulfate Lot No.:_____

Matrix:
a. Water
b. Soil
c. Other_____

Extraction Method:
a. SW-846 3510 (Sep Funnel)
b. SW-846 3550 (Sonication)
c. SW-846 3580 (Waste Dil.)
d. SW-846 3520 (Cont.)
e. SW-846 3541 (Soxhlet)
f. Other:_____

Method Extraction Times:
Start Time:_____
End Time:_____

	Sample #	Sample ID	ICOC	pH[1]			Initial Vol/Wt. (mLs/g)	Final Vol.[2] (mLs)	K-D'd (√)	Clean-Up Absorbent	Multipliers		
											Surr.	Spike	Split
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
12													
13													
14													
15													
16													
17													
18													
19													
20													
21													
22													
23													
24													
25													

[1]Sample pH / Acid Adjusted pH / Base Adjusted pH
[2]The extract volume for BNAs is ~0.8 mLs when the final volume is documented as 1.0 mL. Final volume adjustment is completed in the BNA dept.

___ Insufficient Sample for MS/MSD ___ MS/MSD Not Requested (Limited Vol.) ___ MS/MSD Designated ___MS/MSD Chosen
___ Sample Container Shake ___ Sample Container Shaken & Rinsed with Solvent ___ Sample Container Not Shaken Due To:_____

Comments/Variance:_____

Surrogate:_____ Volume:_____ Std. ID#:_____
LCS/MS Solution:_____ Volume:_____ Std. ID#:_____
LCS/MS Solution:_____ Volume:_____ Std. ID#:_____

Analyst Signature:_____ Date:_____
Reviewer Signature:_____ Date:_____

Extraction Custody Record

Extracts Transferred	Relinquished by	Date	Time	Received by	Date	Time	Reason for Transfer

Analysis Custody Record

Sample(s)	Date/Time Out	Date/Time In	Analyst	Sample(s)	Date/Time Out	Date/Time In	Analyst

Extraction Date:_____ STL Chicago Page No.:_____
Method Code:_____ Organic Extraction Record Batch No.:_____
Solvent:_____ GC Extractables/HPLC Analyst Initials:_____
Solvent Lot No.:_____ Balance ID No.:_____
Solvent Dispenser Volume Checked:_____
Acid / Base (circle & define):_____ Lot No.:_____ Sodium Sulfate Lot No.:_____

Matrix:
a. Water
b. Soil
c. Other_____

Extraction Method:
a. SW-846 3510 (Sep Funnel)
b. SW-846 3550 (Sonication)
c. SW-846 3580 (Waste Dil.)
d. SW-846 3520 (Cont.)
e. SW-846 3541 (Soxhlet)
f. Other_____

Method Extraction Times:
Start Time:_____
End Time:_____

	Sample #	Sample ID	ICOC	pH	Initial Vol/Wt. (mLs/g)	Final Vol.[1] (mLs)	K-D'd (√)	Clean-Up Absorbent	Multipliers		
									Surr.	Spike	Split
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											
21											
22											
23											
24											
25											
26											
27											

[1]The extract volume is ~2.0 mL for Herbicides and 10 mL for TCLP Pesticides. The final volume documented for these extracts, 10 mLs and 100 mLs respectively, reflects the adjusted measures prepared by the instrumentation analysts.

___ Insufficient Sample for MS/MSD ___ MS/MSD Not Requested (Limited Vol.) ___ MS/MSD Designated ___MS/MSD Chosen
___ Sample Container Shaken ___ Sample Container Shaken & Rinsed with Solvent ___ Sample Container Not Shaken Due To:_____

Comments:_____

Surrogate:_____ Volume:_____ Std. ID#:_____
LCS/MS Solution:_____ Volume:_____ Std. ID#:_____
LCS/MS Solution:_____ Volume:_____ Std. ID#:_____

Analyst Signature:_____ Date:_____
Reviewer Signature:_____ Date:_____

Extraction Custody Record

Extracts Transferred	Relinquished by	Date	Time	Received by	Date	Time	Reason for Transfer

Analysis Custody Record

Sample(s)	Date/Time Out	Date/Time In	Analyst	Sample(s)	Date/Time Out	Date/Time In	Analyst

*** BATCH WORKSHEET *** (V2)

Extraction Sep. Funnel (SVOC) Report Date: 7/19/06 14:39

Method Code..: 3510BN	Batch Date...: 07/14/06	QC Code.....:	Equipment Code.:
Batch Code...: 185468	Batch Time...: 713	Calc Code.....: PREPBL	Import Code....:
Status.....: RVWD	User Name....: stw	Location Code..: 57222	

BATCH:	Item	Description	Description Information
	1	Comments	o6gwsbllb
	2	Comments	
	3	Comments	4059 p118
	4	Comments	

SAMPLE:	Grp	Pos	Sample ID	Dilution	SEPFUN Text	MLI mL	MLF mL	PREPF N/A	DLFAC N/A
	1	1	__L_MB__		Complete	1000	1.0	1.0000	1.0000
	1	2	__L_LCS_O6GWLBLKA_		Complete	1000	1.0	1.0000	1.0000
	1	3	__L_LCD_O6GWLBLKA_		Complete	1000	1.0	1.0000	1.0000
	1	4	247619_4_L___		Complete	1060	1.0	0.9434	0.9434
	1	5	247648_1_L___		Complete	1060	1.0	0.9434	0.9434
	1	6	247648_3_L___		Complete	1060	1.0	0.9434	0.9434
	1	7	247660_2____		Complete	620	1.0	1.6129	1.6129
	1	8	247660_3____		Complete	1010	1.0	0.9901	0.9901
	1	9	247660_4____		Complete	1010	1.0	0.9901	0.9901

SAMPLE:	Grp	Pos	Sample ID	Dilution	PH pH Units
	1	1	__L_MB__		
	1	2	__L_LCS_O6GWLBLKA_		
	1	3	__L_LCD_O6GWLBLKA_		
	1	4	247619_4_L___		
	1	5	247648_1_L___		
	1	6	247648_3_L___		
	1	7	247660_2____		
	1	8	247660_3____		
	1	9	247660_4____		

*** BATCH WORKSHEET *** (V2)

Extraction for TCLP (Chlor.Pest) Report Date: 7/19/06 14:59

Method Code..: 3510PT	Batch Date...: 07/18/06	QC Code.....:	Equipment Code.:
Batch Code...: 185644	Batch Time...: 1325	Calc Code.....: PREPT1	Import Code....:
Status.....: RVWD	User Name....: llh	Location Code..: 57222	

BATCH:	Item	Description	Description Information
	1	Comments	o06gpscped
	2	Comments	4061 p 208
	3	Comments	
	4	Comments	

SAMPLE:	Grp	Pos	Sample ID	Dilution	SEPFUN N/A	MLI mL	MLF mL	PREPF N/A	DLFAC N/A
	1	1	__C_MB__		Complete	1000	100.0	10.000	0.100
	1	2	__C_LCS_O6BWLPTFA_		Complete	1000	100.0	10.000	0.100
	1	3	__C_LCS_O6EWLPTTA_		Complete	1000	100.0	10.000	0.100
	1	4	__C_EB1__		Complete	100	100.0	100.000	1.000
	1	5	247569_1_C___		Complete	100	100.0	100.000	1.000
	1	6	247569_1_C_MS_O6BWLPTFA_5		Complete	100	100.0	100.000	1.000
	1	7	247569_1_C_MS_O6EWLPTTA_5		Complete	100	100.0	100.000	1.000
	1	8	247569_2_C___		Complete	100	100.0	100.000	1.000
	1	9	247611_2_C___		Complete	100	100.0	100.000	1.000

Aqueous Extraction Prep Worksheet

Used for Collecting Prep Info)

Batch Number: 500-2989

Analyst: Knieriemen, Dan A

Batch Open: 6/21/2006 10:00:00PM

Method Code: 500-3510C-500

Batch End: 6/21/2006 11:00:00PM

Separatory Funnel Liquid-Liquid Extraction

	Input Sample Lab ID	Input Sample Lab ID (Analytical Method)	SDG	GrossWt TareWt	InitAmnt FinAmnt	PHs Rcvd	PHs Adj1	PHs Adj2	Due Date	Analytical TAT	Dlv Rank	Comments
1	MB 500-2989/1	MB~500-2989/1 N/A	N/A		1000 mL 10.0 mL				N/A	N/A	N/A	
2	LCS 500-2989/2	LCS~500-2989/2 N/A	N/A		1000 mL 10.0 mL				N/A	N/A	N/A	
3	LCSD 500-2989/3	LCSD~500-2989/3 N/A	N/A		1000 mL 10.0 mL				N/A	N/A	N/A	
4	LCS 500-2989/4	LCS~500-2989/4 N/A	N/A		1000 mL 10.0 mL				N/A	N/A	N/A	
5	LCSD 500-2989/5	LCSD~500-2989/5 N/A	N/A		1000 mL 10.0 mL				N/A	N/A	N/A	
6	500-493-A-1	500-493-A-1 (8081A)	N/A		700 mL 10.0 mL				6/30/06	10_Days	1	
6	500-493-A-1	500-493-A-1 (8082)	N/A		700 mL 10.0 mL				6/30/06	10_Days	1	

Aqueous Extraction Prep Worksheet

Used for Collecting Prep Info)

Batch Number: 500-2989 Analyst: Knieriemen, Dan A Batch Open: 6/21/2006 10:00:00PM

Method Code: 500-3510C-500 Batch End: 6/21/2006 11:00:00PM

Batch Notes

Acid used for pH adjustment	
Base used for pH adjustment	
Batch Comment	
Person's name who did the concentration	
First End time	
Vendor lot number	
Na2SO4 Lot Numer	
Oven, Bath or Block Temperature 1	
Prep Solvent Volume Used	
Person's name who did the prep	
Person's name who witnessed reagent drop	
Solvent	
SOP Number	
First Start time	

Comments

Login Comments for Job 493: LIVE

Aqueous Extraction Prep Worksheet

Used for Collecting Prep Info)

Batch Number: 500-2989 Analyst: Knieriemen, Dan A Batch Open: 6/21/2006 10:00:00PM

Method Code: 500-3510C-500 Batch End: 6/21/2006 11:00:00PM

Reagent Additions Worksheet

Lab ID	Reagent Code	Amount Added	Final Amount	By	Witness
MB 500-2989/1	EXCPPSUW_00023	1000 uL	10.0 mL		
LCS 500-2989/2	EXCPPSPW_00008	1000 uL	10.0 mL		
LCS 500-2989/2	EXCPPSUW_00023	1000 uL	10.0 mL		
LCSD 500-2989/3	EXCPPSPW_00008	1000 uL	10.0 mL		
LCSD 500-2989/3	EXCPPSUW_00023	1000 uL	10.0 mL		
LCS 500-2989/4	EXCPPSUW_00023	1000 uL	10.0 mL		
LCS 500-2989/4	EXPCBSPW66_00005	1.0 mL	10.0 mL		
LCSD 500-2989/5	EXCPPSUW_00023	1000 uL	10.0 mL		
LCSD 500-2989/5	EXPCBSPW66_00005	1.0 mL	10.0 mL		
500-493-A-1	EXCPPSUW_00023	1000 uL	10.0 mL		

Aqueous Extraction Prep Worksheet

Used for Collecting Prep Info)

Batch Number: 500-2989 Analyst: Knieriemen, Dan A Batch Open: 6/21/2006 10:00:00PM

Method Code: 500-3510C-500 Batch End: 6/21/2006 11:00:00PM

Other Reagents:

Reagent	Amount/Units	Lot#:

Aqueous Extraction Prep Worksheet

Used for Collecting Prep Info)

Batch Number: 500-2940 Analyst: Rutnicki, Debbie L Batch Open: 6/22/2006 5:00:25PM

Method Code: 500-3510C-500 Batch End: 6/22/2006 11:00:00PM

Separatory Funnel Liquid-Liquid Extraction

	Input Sample Lab ID	Input Sample Lab ID (Analytical Method)	SDG	GrossWt TareWt	InitAmnt FinAmnt	PHs Rcvd	PHs Adj1	PHs Adj2	Due Date	Analytical TAT	Dlv Rank	Comments
1	MB 500-2940/1	MB~500-2940/1 N/A	N/A		1000 mL 5.0 mL	6			N/A	N/A	N/A	
2	LCS 500-2940/2	LCS~500-2940/2 N/A	N/A		1000 mL 5.0 mL	6			N/A	N/A	N/A	
3	LCSD 500-2940/3	LCSD~500-2940/3 N/A	N/A		1000 mL 5.0 mL	6			N/A	N/A	N/A	
4	500-502-H-1	500-502-H-1 (8015B_DRO)	N/A		930 mL 5.0 mL	6			7/5/06	10_Days	2	
5	500-502-H-2	500-502-H-2 (8015B_DRO)	N/A		890 mL 5.0 mL	6			7/5/06	10_Days	2	
6	500-502-H-3	500-502-H-3 (8015B_DRO)	N/A		930 mL 5.0 mL	6			7/5/06	10_Days	2	
7	500-502-H-5	500-502-H-5 (8015B_DRO)	N/A		930 mL 5.0 mL	6			7/5/06	10_Days	2	
8	500-502-H-6	500-502-H-6 (8015B_DRO)	N/A		1000 mL 5.0 mL	6			7/5/06	10_Days	2	
9	500-502-H-7	500-502-H-7 (8015B_DRO)	N/A		950 mL 5.0 mL	6			7/5/06	10_Days	2	

Aqueous Extraction Prep Worksheet

Used for Collecting Prep Info)

Batch Number: 500-2940 Analyst: Rutnicki, Debbie L Batch Open: 6/22/2006 5:00:25PM

Method Code: 500-3510C-500 Batch End: 6/22/2006 11:00:00PM

Batch Notes

Acid used for pH adjustment	
Base used for pH adjustment	
Batch Comment	
Person's name who did the concentration	
First End time	
Vendor lot number	
Na2SO4 Lot Numer	
Oven, Bath or Block Temperature 1	
Prep Solvent Volume Used	
Person's name who did the prep	
Person's name who witnessed reagent drop	
Solvent	
SOP Number	
First Start time	

Comments

Login Comments for Job 502: LIVE

Aqueous Extraction Prep Worksheet

Used for Collecting Prep Info)

Batch Number: 500-2940 Analyst: Rutnicki, Debbie L Batch Open: 6/22/2006 5:00:25PM

Method Code: 500-3510C-500 Batch End: 6/22/2006 11:00:00PM

Reagent Additions Worksheet

Lab ID	Reagent Code	Amount Added	Final Amount	By	Witness
MB 500-2940/1	EXDROSUW_00005	500 uL	5.0 mL		
LCS 500-2940/2	EXDROSPW_00003	500 uL	5.0 mL		
LCS 500-2940/2	EXDROSUW_00005	500 uL	5.0 mL		
LCSD 500-2940/3	EXDROSPW_00003	500 uL	5.0 mL		
LCSD 500-2940/3	EXDROSUW_00005	500 uL	5.0 mL		
500-502-H-1	EXDROSUW_00005	500 uL	5.0 mL		
500-502-H-2	EXDROSUW_00005	500 uL	5.0 mL		
500-502-H-3	EXDROSUW_00005	500 uL	5.0 mL		
500-502-H-5	EXDROSUW_00005	500 uL	5.0 mL		
500-502-H-6	EXDROSUW_00005	500 uL	5.0 mL		
500-502-H-7	EXDROSUW_00005	500 uL	5.0 mL		

Aqueous Extraction Prep Worksheet

Used for Collecting Prep Info)

Batch Number: 500-2940 Analyst: Rutnicki, Debbie L Batch Open: 6/22/2006 5:00:25PM

Method Code: 500-3510C-500 Batch End: 6/22/2006 11:00:00PM

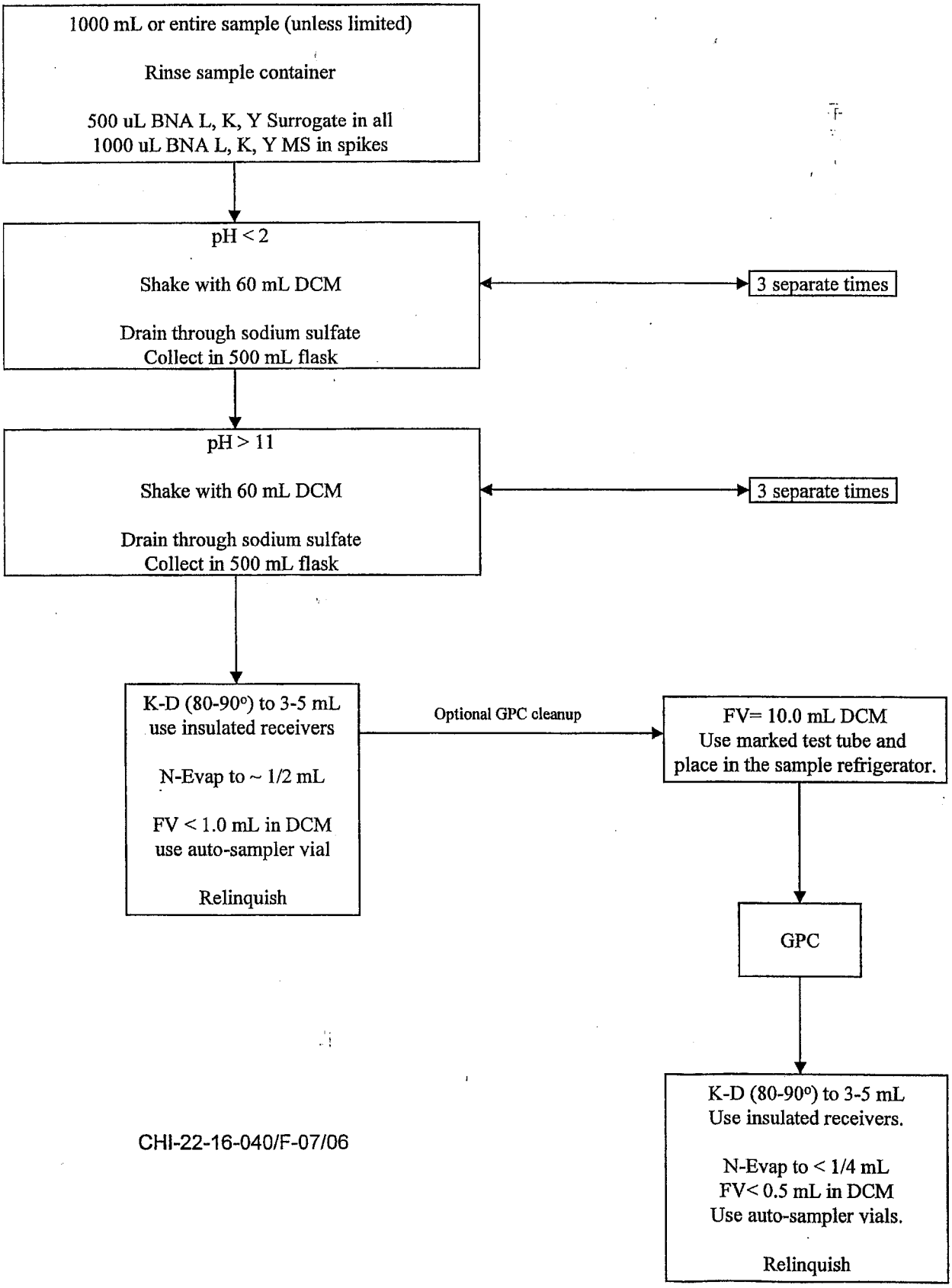
Other Reagents:

Reagent	Amount/Units	Lot#:

Attachment 2.

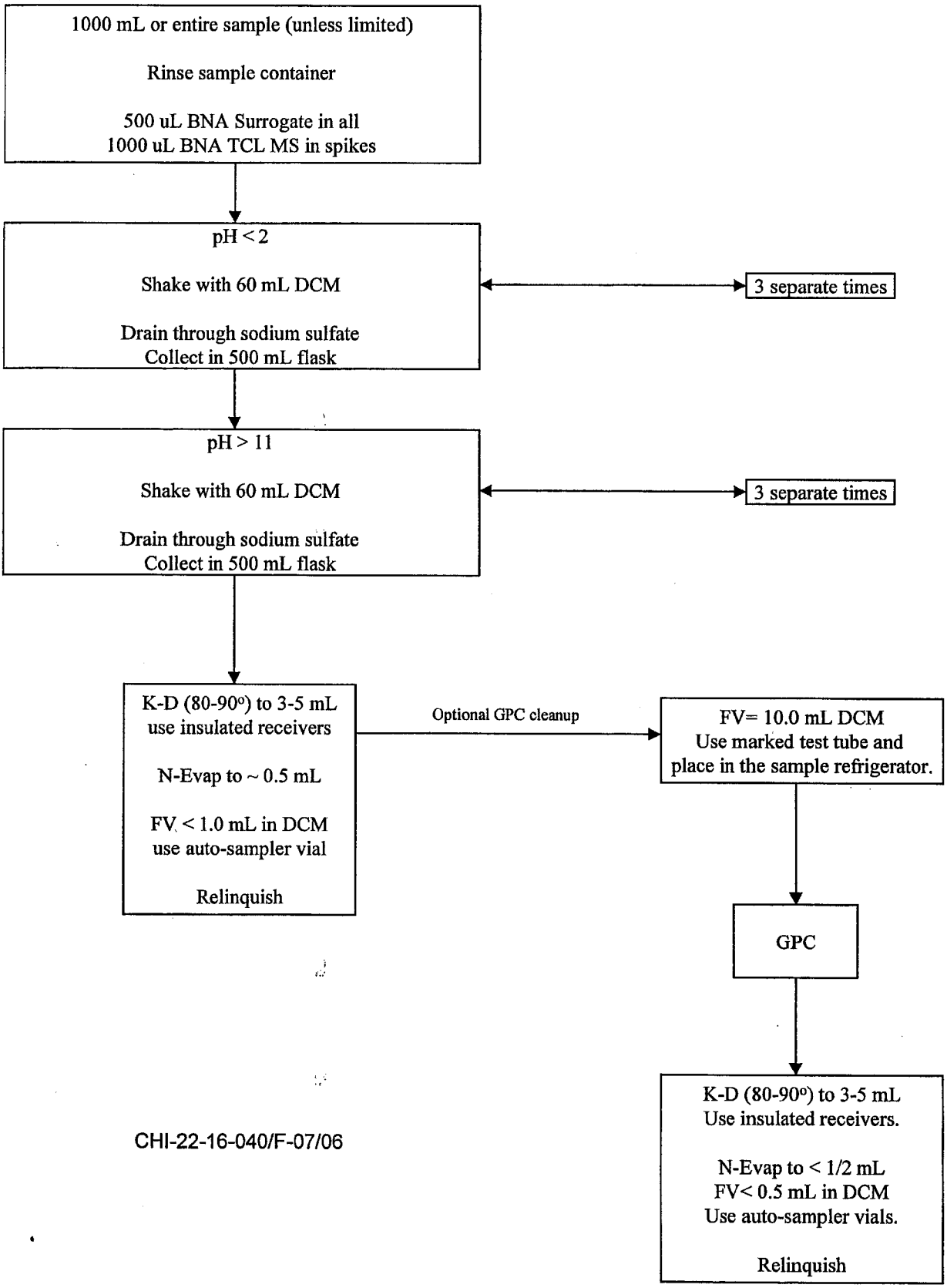
Example: Procedural Flowcharts

Flowchart for BNA Water (8270C, 625)
by 3510C
3510BN 'L' Matrix



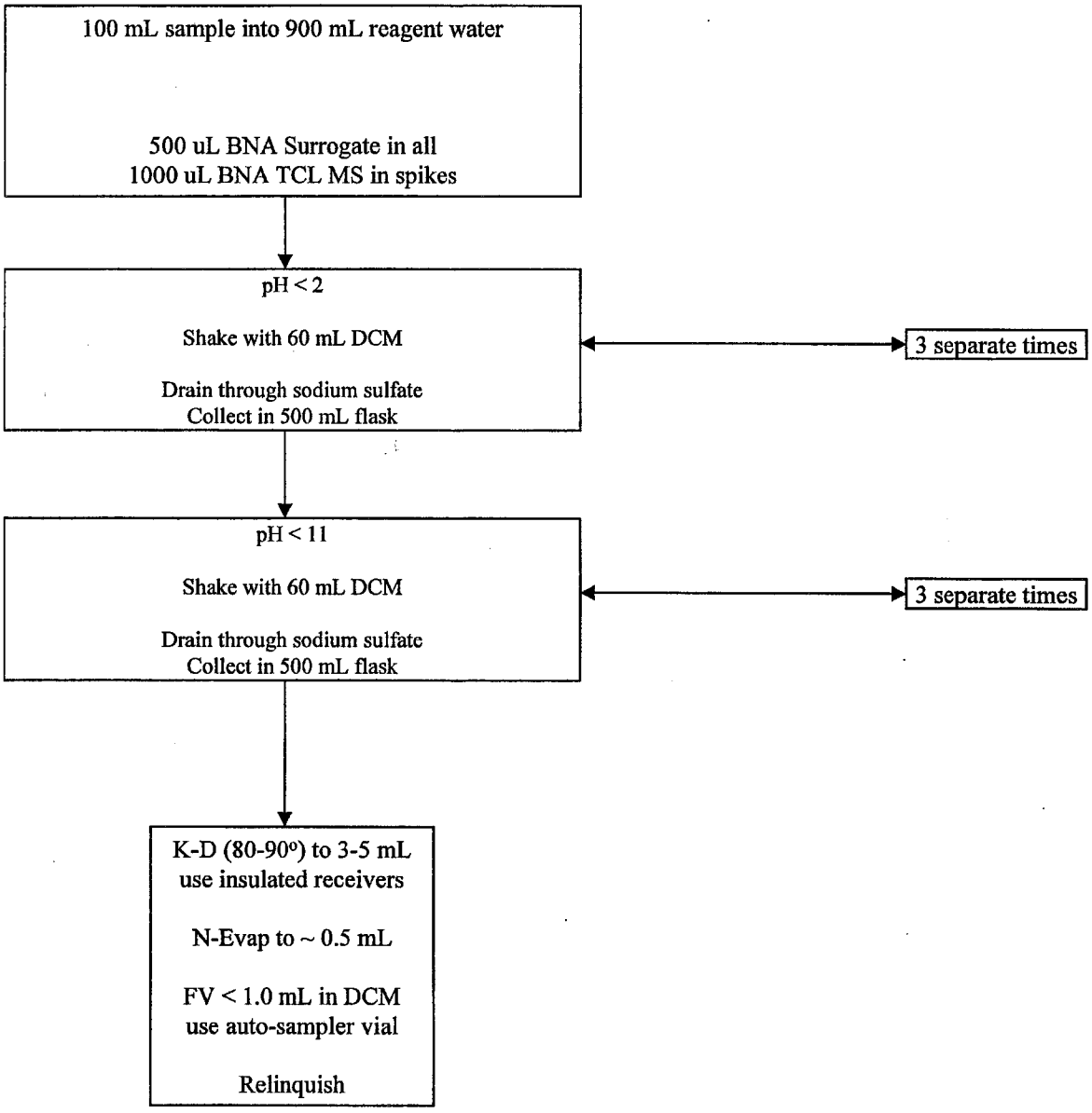
CHI-22-16-040/F-07/06

Flowchart for BNA Water (8270C, 625)
by 3510C
3510BN, 625X



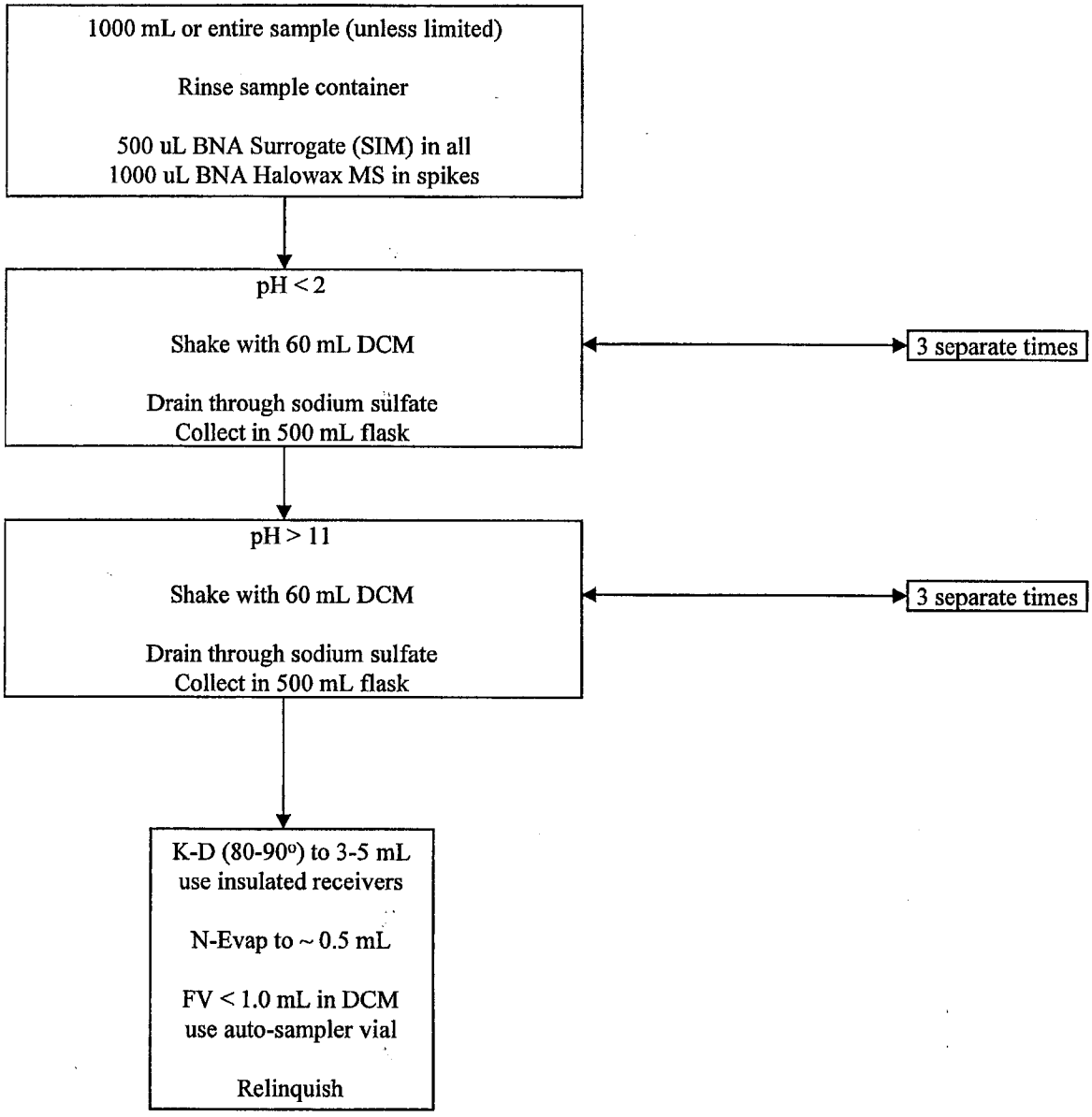
CHI-22-16-040/F-07/06

Flowchart for BNA TCLP
by 3510C
3510BT



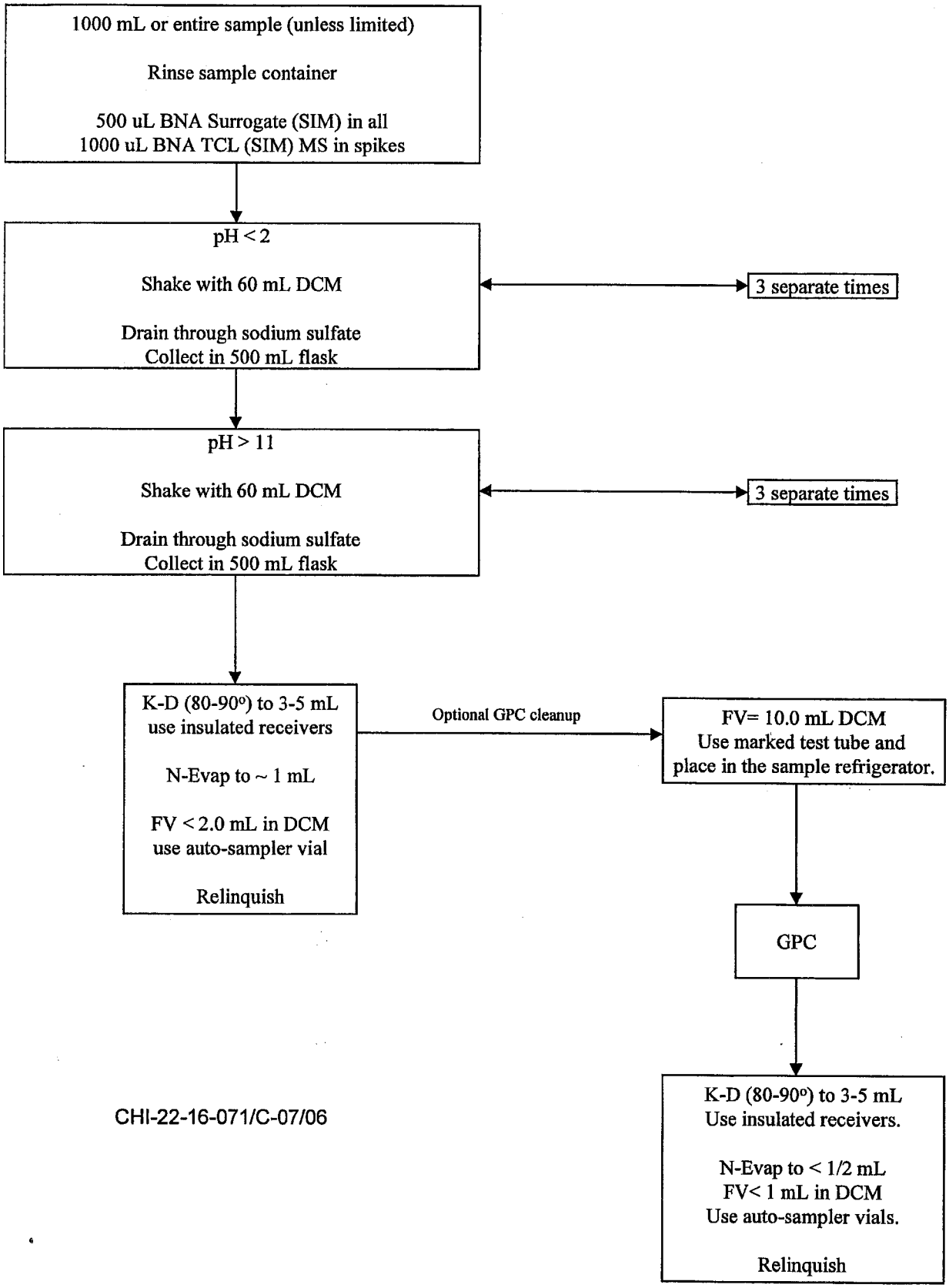
CHI-22-16-062/D-07/06

Flowchart for BNA Halowax Water
by 3510C
3510BH



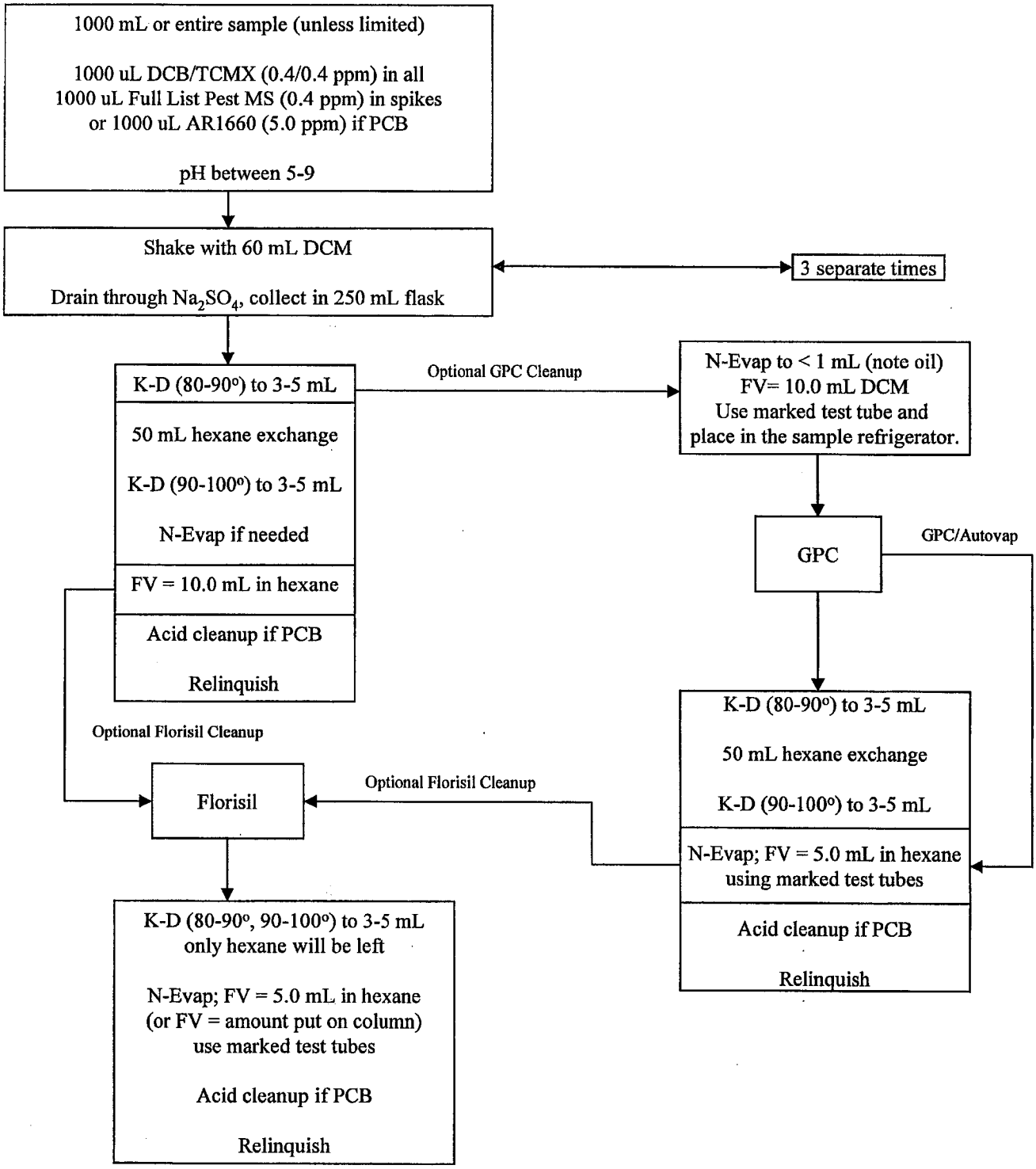
CHI-22-16-070/C-07/06

Flowchart for BNA SIM Water
by 3510C
3510BS



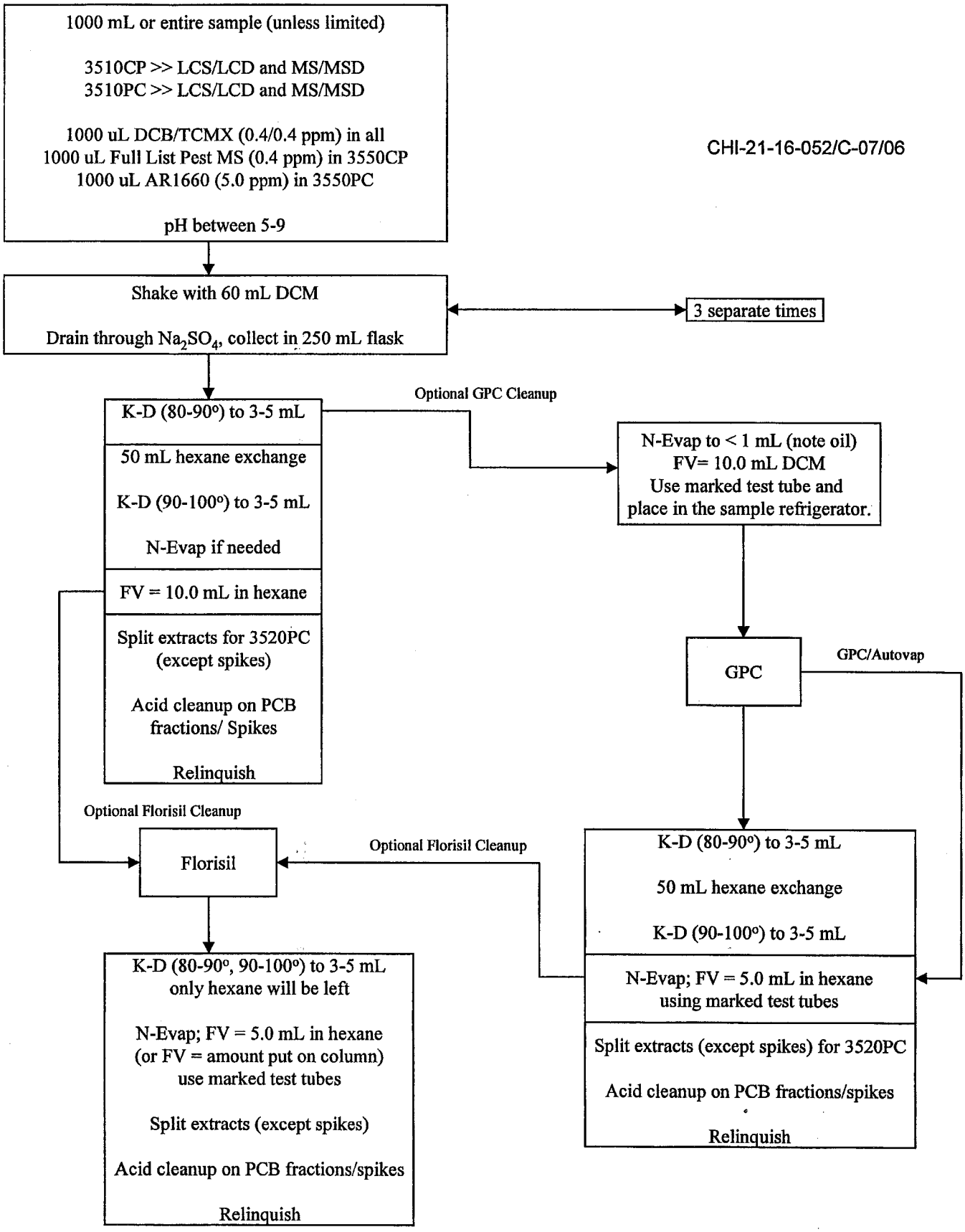
CHI-22-16-071/C-07/06

Flowchart for Pest/PCB Water (8081, 8082, 608)
by 3510
3510CP, 3510PC, 608X

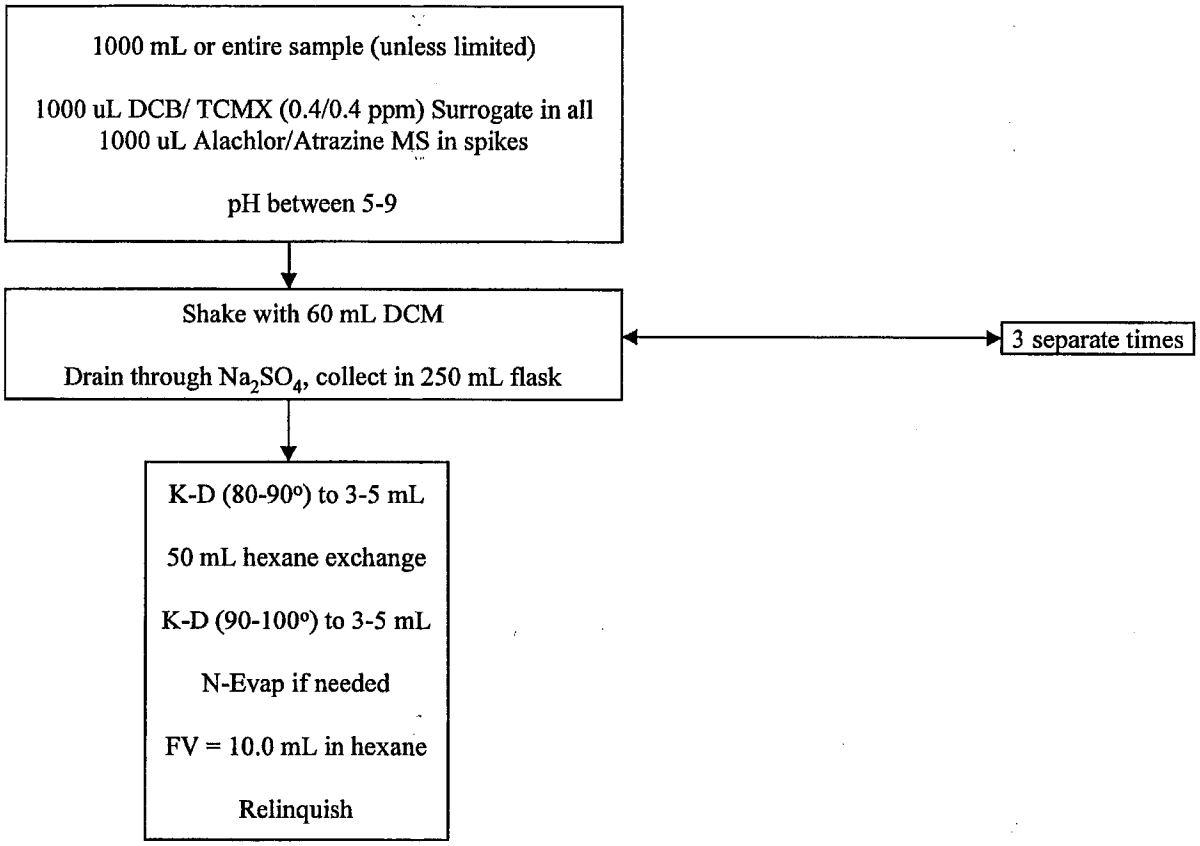


CHI-22-16-036/D-07/06

Flowchart for Pest/PCB Water (8081, 8082)
by 3510
3510CP, 3510PC, HYDPPW combined

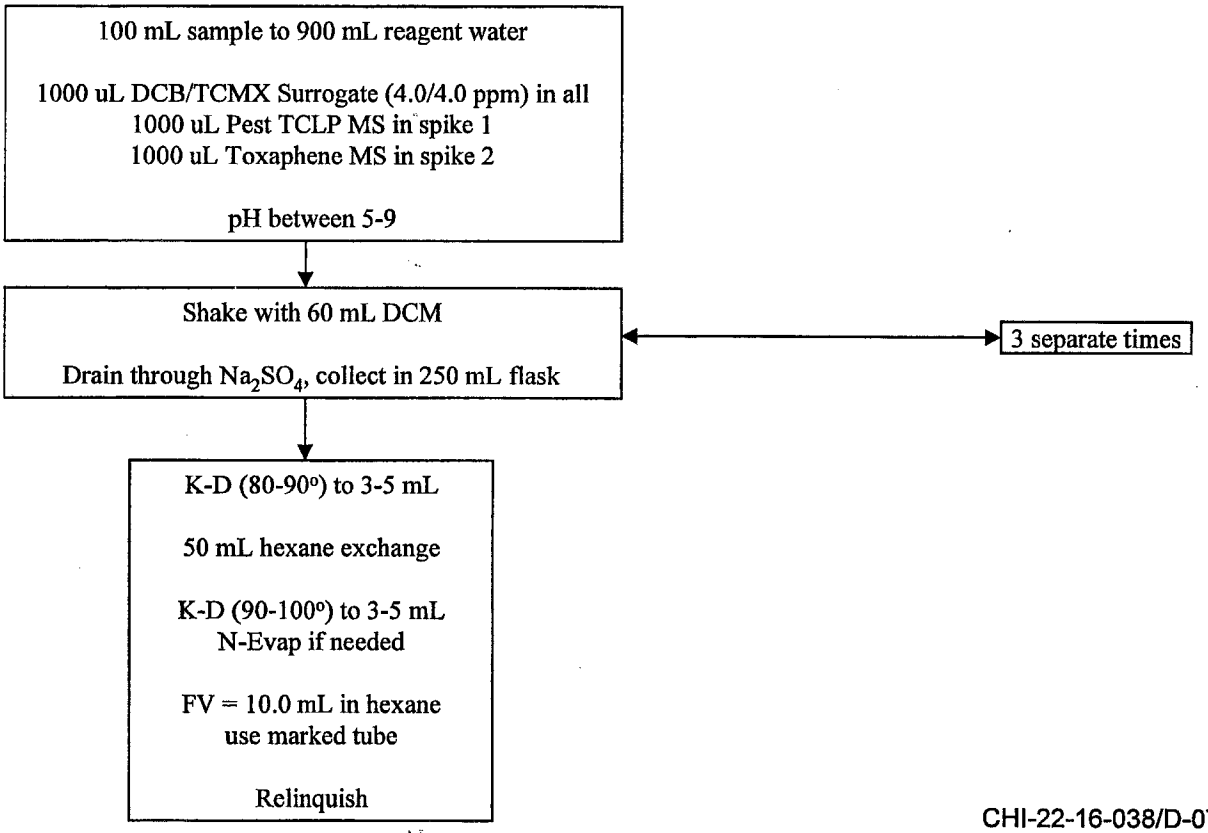


Flowchart for Alachlor/Atrazine Water (8081A)
by 3510C
3510AA



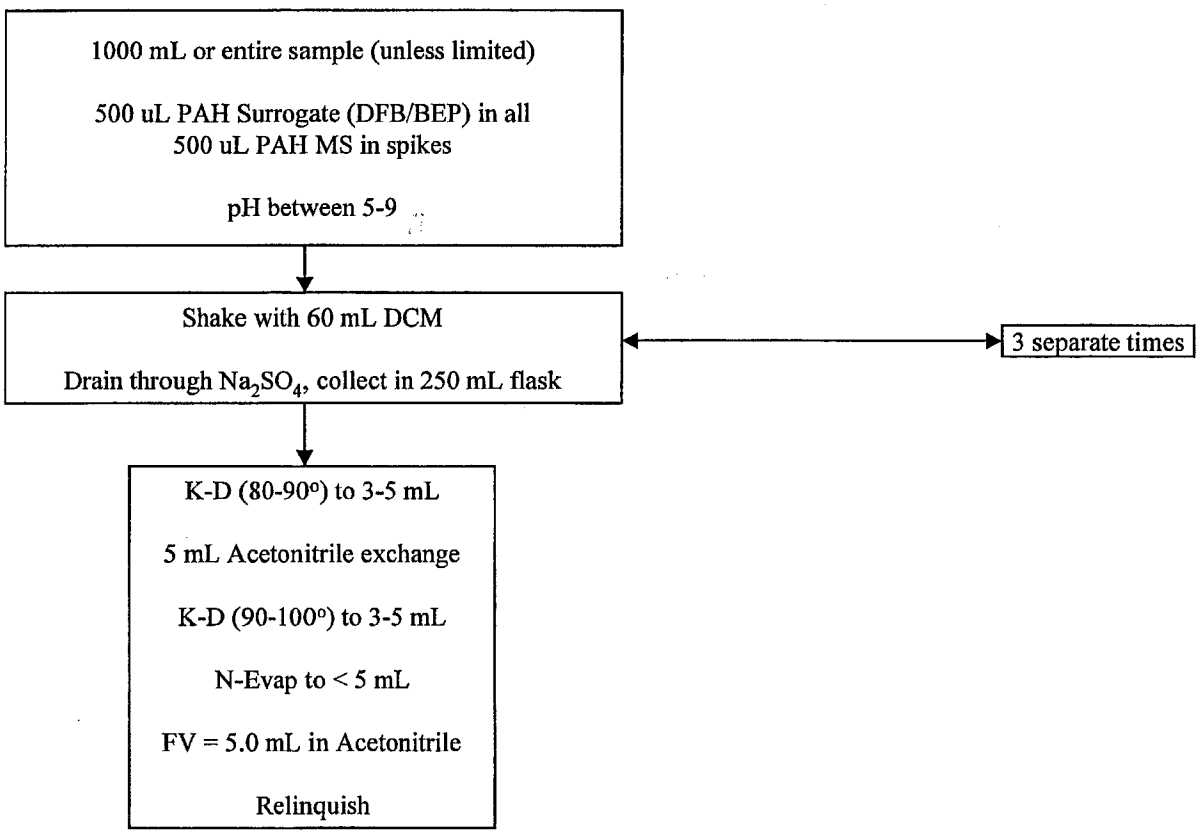
CHI-22-16-069/B-07/06

Flowchart for Pest/PCB TCLP
by 3510
3510PT



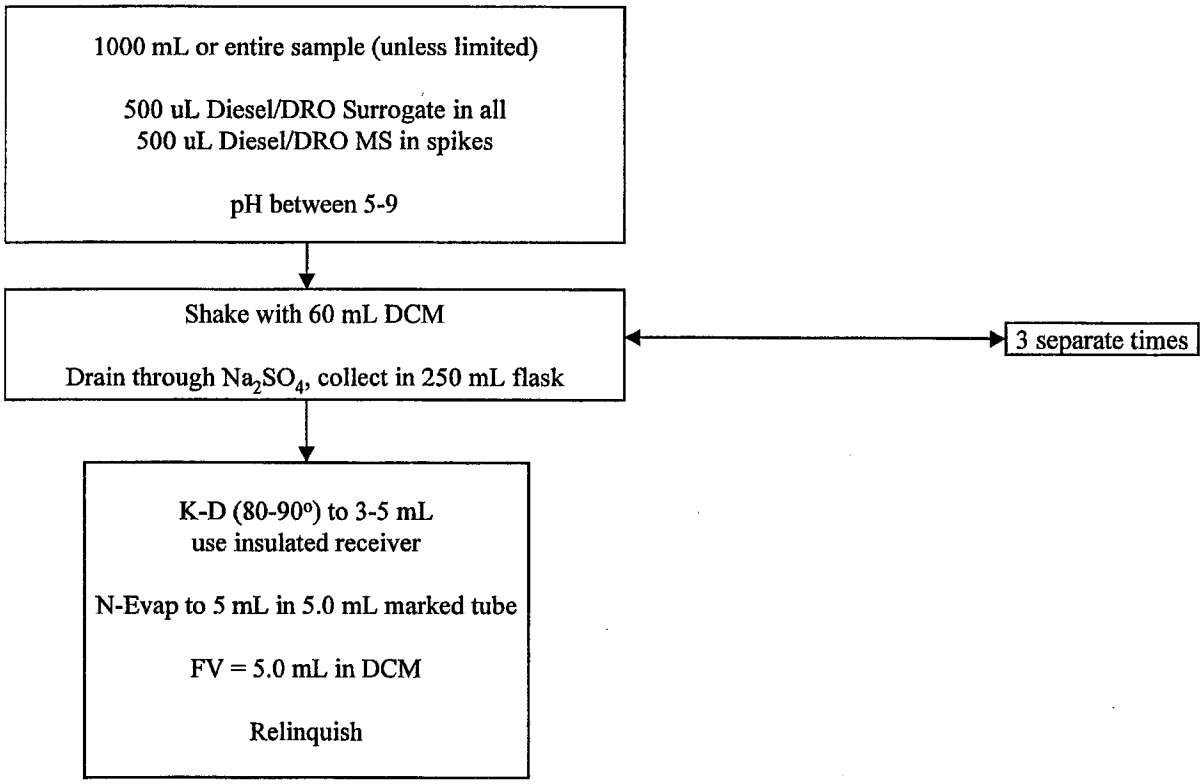
CHI-22-16-038/D-07/06

Flowchart for PAH Water (8310, 610)
by 3510
3510PN, 610X



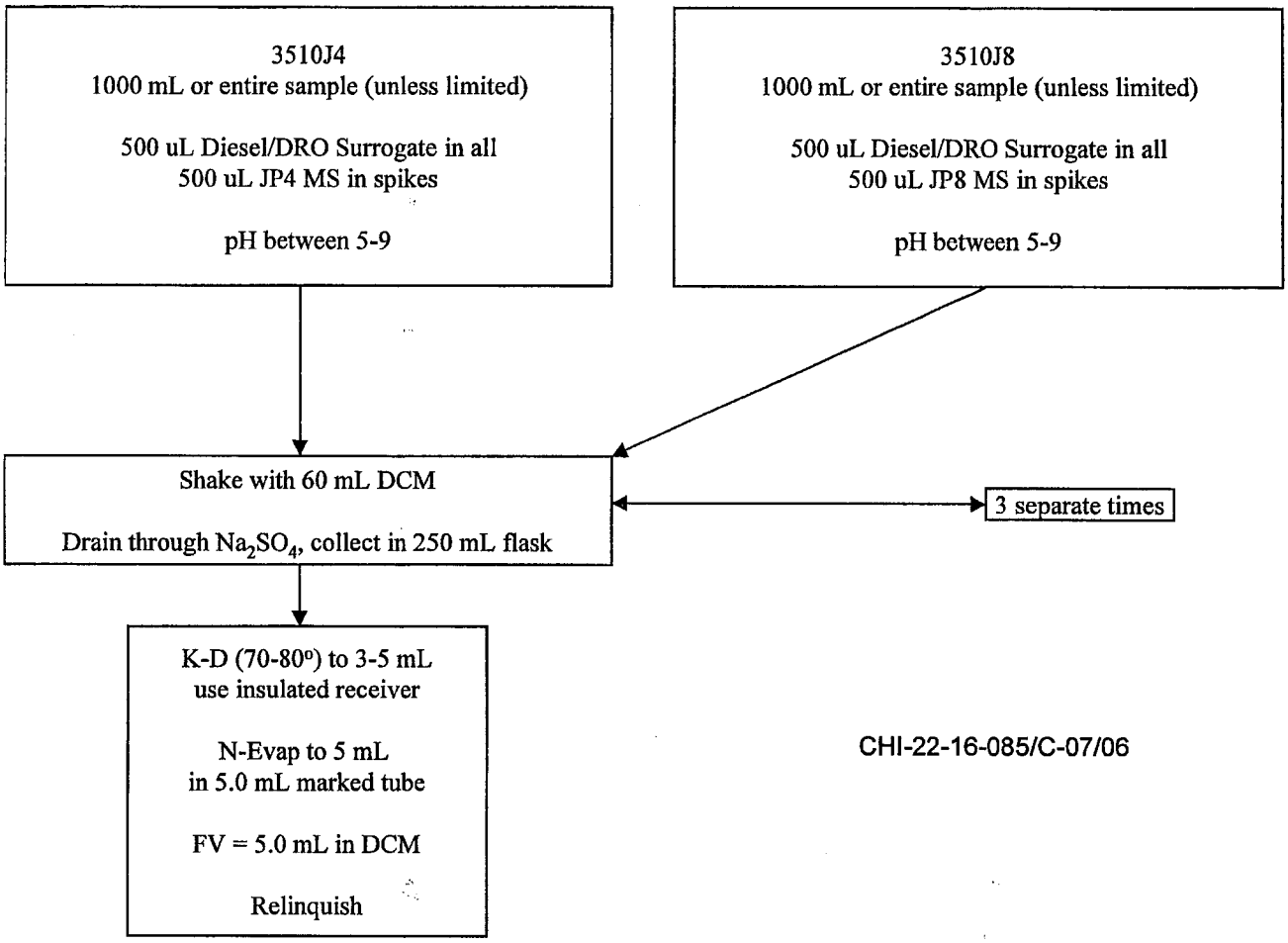
CHI-22-16-031/D-07/06

Flowchart for DRO Water (CA Method)
by 3510
3510D



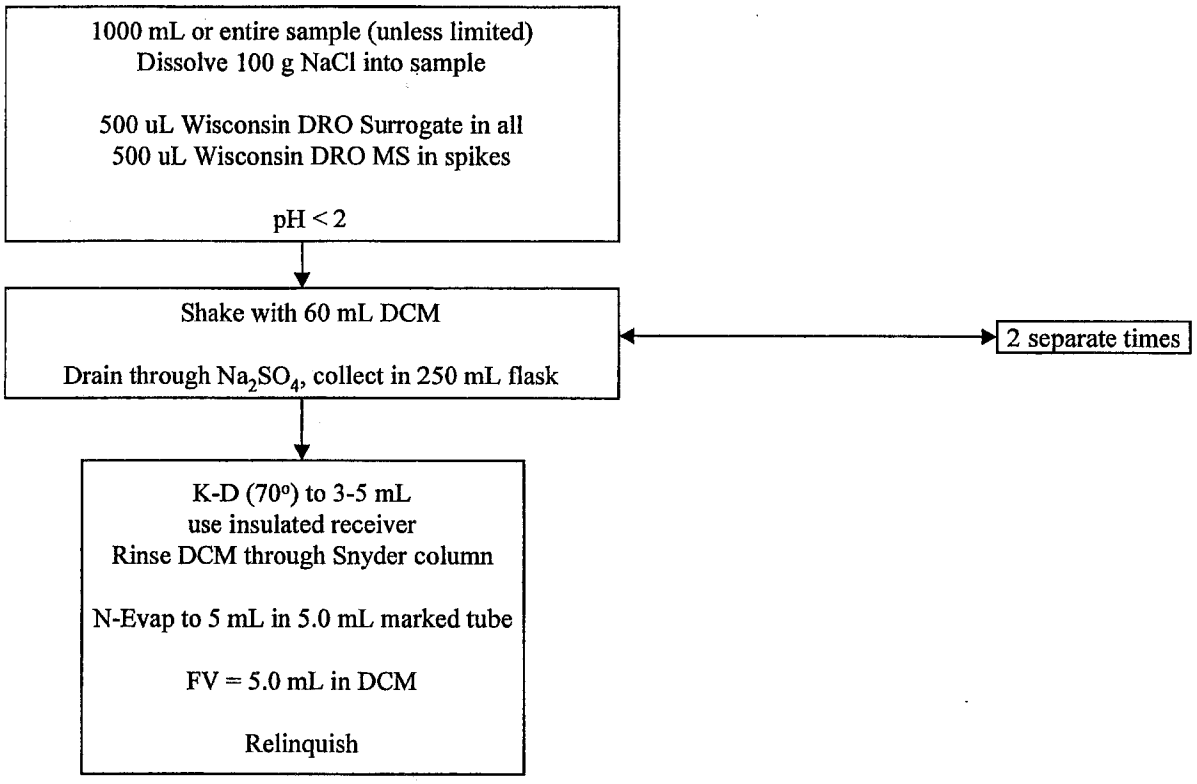
CHI-22-16-064/C-07/06

Flowchart for JP4 Water
by 3510
3510J4/3510J8



CHI-22-16-085/C-07/06

Flowchart for Wisconsin DRO Water
by 3510
WIDROW



CHI-22-16-098/B-07/06

Appendix 1

BNA Halowax

Other than having different standards, the BNA Halowax extraction is identical to the BNA separatory funnel procedure.

1.0 Surrogate and Matrix Spike Solutions

1.1 BNA Surrogate Spike (SIM) Solution

The surrogate used for the halowax extraction is the same solution used for the BNA SIM extraction. The BNA Surrogate Spike (SIM) Solution is prepared from the BNA Surrogate Spike at the levels listed below. 500 uLs of BNA Surrogate (SIM) Spike Solution is added to all samples, MBs, LCS and MS/MSDs.

Compound	Concentration (ug/mL)
p-Terphenyl-d_4	10
Nitrobenzene-d_5	10
2-Fluorobiphenyl	10
1,2-Dichlorobenzene-d_4	10
Phenol-d_5	15
2-Fluorophenol	15
2,4,6-Tribromophenol	15
2-Chlorophenol-d_4	15

- Life of Standard: 6-months from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2

1.2 BNA Halowax Matrix Spike Solution

The BNA Halowax Matrix Spike Solution is prepared by the BNA analytical group. The composition and concentration of this standard is beyond the scope of this SOP. See the analytical SOP for specifics about this standard. 1000 uLs of the matrix spike solution is added to the LCS and MS/MSD.

- Life of Standard: 6-months from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2

Appendix 2

Alachlor/Atrazine

Other than having different standards, the Alachlor/Atrazine extraction is identical to the pesticide separatory funnel procedure.

1.0 Surrogate and Matrix Spike Solutions

1.1 Pesticide/PCB Surrogate Spike Solution

The surrogate used for the Alachlor and Atrazine extraction is the same solution used for the pesticides/PCBs extraction. The surrogate used in the extraction of pesticides/PCBs from waters is a solution of Decachlorobiphenyl (DCB) and 2,4,5,6-Tetrachloro-m-xylene (TCX) in acetone at the concentrations listed below. 1,000 uLs of Pesticide/PCB Surrogate Spike Solution is added to all samples, MBs, LCS and MS/MSD.

Compound	Concentration (ug/mL)
DCB	0.4
TCX	0.4

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

1.2 Alachlor/Atrazine Matrix Spike Solution

The LCS/MS solution used in the extraction Alachlor and Atrazine from waters is a solution in methanol. The composition and concentration of this standard is beyond the scope of this SOP. See the analytical SOP for specifics about this standard. 1,000 uLs of Alachlor/Atrazine Spike Solution is added to LCS and MS/MSD.

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

Appendix 3

Wisconsin DRO

In addition using specific surrogate and spike solutions, the Wisconsin DRO extraction differs from the SW-846 DRO extraction. The changes are noted in this appendix.

1.0 Reagents

1.1 Heat-Purified Sodium Chloride

Sodium chloride purchased directly from vendor. Purify by heating at 400°C for four hours in a shallow drying tray, cool in a desiccator, and store in a glass bottle.

- Life of Reagent: 1-year.
- Storage Requirements: Store in a glass container and keep dry (anhydrous).

2.0 Surrogate and Matrix Spike Solutions

2.1 Wisconsin DRO Surrogate Solution

The Wisconsin DRO surrogate solution is prepared by the DRO analyst at the levels listed below. 500 uLs of the surrogate is added to all samples, MBs, LCS/LCD and MS/MSDs.

Compound	Concentration (ug/mL)
C9-Nonane	100

- Life of Standard: 6-months from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2

2.2 Wisconsin DRO Matrix Spike Solution

The Wisconsin DRO Matrix Spike Solution is prepared by the DRO analyst. The composition and concentration of this standard is beyond the scope of this SOP. See the analytical SOP for specifics about this standard. 500 uLs of the matrix spike solution is added to the LCS/LCD and MS/MSD.

- Life of Standard: 6-months from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2

3.0 Wisconsin DRO Extraction

3.1 Clarification of section MB and LCS water preparation in **7.6.1**. Add 1.0 liter of Milli-Q water to 3 separatory funnels and label as the MB, LCS and LCD. A LCD must be extracted even if there is a MS/MSD.

3.2 Add to section **7.6.3**. Samples should be preserved in the field. If sample pH is greater than two, sample results must be flagged.

3.3 Add to section **7.6.4**. Add 100 g NaCl to separtory funnel, then shake. Ensure that the salt is dissolved into sample before adding surrogate and spike.

3.4 In section **7.6.11**, repeat the extraction only once more for a total of two, 60 mL extractions.

3.5 Make the following changes in section **7.6.12.1**. Use the 10 mL insulated concentrator tubes. The K-D bath should be at 70° C.

3.6 In section **7.6.12**, add rinse a small amount of DCM through the Snyder column before removing it from the K-D flask.

3.7 Refer to Diesel/DRO section in **7.6.13**.

Appendix 4

JP4 and JP8

Other than having different standards, the JP4 or JP8 extraction is identical to the DRO separatory funnel procedure.

1.0 Surrogate and Matrix Spike Solutions

1.1 DRO Surrogate Spike Solution

The surrogate used for the JP4 or JP8 extraction is the same solution used for the DRO extraction. The surrogate used in the extraction of DRO from waters is a solution of 2-Fluorobiphenyl and o-Terphenyl in acetone at the concentrations listed below. The GC group prepares the working surrogate solution. 500 uLs of DRO Surrogate Spike Solution is added to all samples, MBs, LCS and MS/MSD.

Compound	Concentration (ug/mL)
2-Fluorobiphenyl	100
o-Terphenyl	100

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

1.2 JP4 Matrix Spike Solution

The LCS/MS solution used in the extraction of JP4 from waters is a solution in methanol. The composition and concentration of this standard is beyond the scope of this SOP. See the analytical SOP for specifics about this standard. 500 uLs of JP4 Spike Solution is added to LCS and MS/MSD.

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

1.2 JP8 Matrix Spike Solution

The LCS/MS solution used in the extraction of JP8 from waters is a solution in methanol. The composition and concentration of this standard is beyond the scope of this SOP. See the analytical SOP for specifics about this standard. 500 uLs of JP8 Spike Solution is added to LCS and MS/MSD.

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

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TITLE: SAMPLE PREPARATION Semivolatile and Nonvolatile Organic Compounds from a Soil/Sediment Matrix Using Soxhlet Extraction

Updated by:	Signature:	Date
Daniel A. Knieriemen Supervisor, Organic Extractions		08/17/06

Approved by:	Signature:	Date
Daniel A. Knieriemen Supervisor, Organic Extractions		08/17/06
David W. Mazur Env. Health & Safety Coor.		8/17/06
Terese A. Preston Quality Manager	Terese A. Preston	8/17/06

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1.0 SCOPE AND APPLICATION

This SOP outlines the extraction procedure of semivolatile and nonvolatile compounds [1] from soil and sediment matrices using SW-846 Method 3541. The compounds of interest are as listing in the analytical Standard Operating Procedure (SOP).

[1] BNAs, Pesticides, Pesticides/PCBs, PCBs, PAHs, and DROs.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Reporting Limits

Not Applicable - Refer to the analytical SOPs.

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.2 Summary of Method

Soil and sediment samples are prepared for subsequent analysis. Approximately 15 grams of sample is dried with sodium sulfate and extracted using Automated Soxhlet Extraction with Hexane:Acetone (1:1) or DCM:Acetone (1:1) as the extraction solvent. The extract is dried and concentrated and exchanged into hexane. The extracts are stored at 4 ± 2°C prior to analysis.

2.0 INTERFERENCES

- Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.
- Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic material. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials.
- Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

- Take careful note of those sections marked "CAUTION" and "NOTE".
- DCM is considered a health hazard and possible carcinogen. It is harmful if swallowed or inhaled. The vapor is irritating, and thus should be used in a hood. It is readily absorbed through the skin and contact may be irritating.
- PCBs are a bio-accumulating carcinogen. Extreme care should be taken when working with these standards and samples.
- All glassware should be carefully inspected for any kind of crack or star prior to use. An imperfect separatory funnel could explode from the pressure that builds up when solvent is added. Dispose of imperfect glassware in an appropriate container. Some types of glassware are repairable.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit [1]	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Acetonitrile	Flammable Poison	40 ppm-TWA	Early symptoms may include nose and throat irritation, flushing of the face, and chest tightness. Prolonged exposure to high levels of vapors may cause formation of cyanide anions in the body.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.

[1] Exposure limit refers to the OSHA regulatory exposure limit.

4.0 EQUIPMENT AND SUPPLIES

4.1 Glassware

- 100 mL, 2000 mL graduated cylinder
- 1.0, 10.0 mL volumetric pipet, Class A
- 10 mL graduated centrifuge tubes
- transfer pipets
- 100 mL beakers
- Glass extraction thimble and beaker (Soxtherm)
- 100 mL class A volumetric flask
- Test tubes with Teflon-lined, screw-top caps

4.2 Miscellaneous

- Nitrogen Evaporator
- Centrifuge
- Automated Soxhlet Extraction Unit (Soxtherm Unit, O.I. Analytical)
- Waterbath - heated, with concentric ring covers, capable of temperature control. Bath must be in hood.
- Magnetic stir plate and stir bars
- Wide range pH paper 1 to 12
- Boiling Chips; soxhlet extracted
- Stainless steel spatula
- Muffle furnace
- Desiccator
- Balance
- 70 mm Whatman 541 Filter Paper

5.0 Reagents and Standards

A label on any reagent bottle must contain the concentration of the reagent, name of the reagent, date prepared, expiration date and the analyst who prepared the reagent.

5.1 Reagents

5.1.1 Solvents

Acetone; Hexane; Methanol; Methylene Chloride [a.k.a., Dichloromethane (DCM)] - Pesticide quality or better.

5.1.2 Heat Purified Granular Sodium Sulfate

Purify by heating at 400°C for 4-hours in a shallow drying tray, cool in a desiccator, and store in a glass bottle.

- Life of Reagent: 1-year.
- Storage Requirements: Store in a glass container with a tight fitting closure preventing any contact with water. It must remain dry (anhydrous).

5.1.3 Heat Purified Powdered Sodium Sulfate

Purify by heating at 400°C for 4-hours in a shallow drying tray, cool in a desiccator, and store in a glass bottle.

- Life of Reagent: 1-year.
- Storage Requirements: Store in a glass container with a tight fitting closure preventing any contact with water. It must remain dry (anhydrous).

5.1.4 DCM:Acetone (1:1) (v:v)

Add 1000 mLs pesticide grade DCM into 1000 mLs of pesticide grade acetone in a 2-L graduated cylinder. Pour into a clean labeled 4-L solvent bottle.

- Hazardous Properties: Acetone is flammable. When not in use, it should be stored in a flammable cabinet. Do not use near an open flame or heat. DCM is an inhalation hazard. Use only in a well ventilated area. Harmful if swallowed.
- Life of Reagent: 1-year.
- Storage Requirements: Store in a glass container with a Teflon-lined cap. Store in a flammable cabinet.

5.1.5 Hexane : Acetone (1:1) (v:v)

Add 1000 mLs of pesticide grade acetone into 1000 mLs of pesticide grade hexane in a 2-L graduated cylinder. Pour into a clean, labeled 4-L solvent bottle.

- Hazardous Properties: Acetone and hexane are flammable. When not in use, it should be stored in a flammable cabinet. Do not use near an open flame or heat. Use only in a well ventilated area. Harmful if swallowed.
- Life of Reagent: 1-year.
- Storage Requirements: Store in a glass container with a Teflon-lined cap. Store in a flammable cabinet.

5.2 Quality Control (QC) Solutions

QC solutions must be stored in amber or foil-wrapped, glass containers that have Teflon-lined caps. The label on the container must contain the following information: Name of the solution, standard number, concentration of the components, date prepared, preparation analyst, and expiration date. All QC solutions are stored either in the standards refrigerator in the GC/MS lab, GC extractables lab, or in the standards refrigerator located in the organic extraction lab. QC solutions are stored at $4 \pm 2°C$.

Listed below are the various QC solutions and concentrations appropriate for extraction of BNAs, Pesticides, Pesticides/PCBs, PCBs, PAHs, and Diesel/DRO from soil/sediment matrices. Instructions detailing the preparation of these solutions are found in the corresponding analytical SOPs.

5.2.1 Surrogate Spike Solution

5.2.1.1 BNA Surrogate Spike Solution

The BNA Surrogate Spike Stock Solution is purchased directly from a chemical vendor at 10 times the concentration of the levels listed below. See Attachment 3. The BNA Surrogate Spike Working Solution is prepared by pipetting 10.0 mLs of BNA Surrogate Spike Stock Solution to a 100.0 mL flask. Class A glassware must be used. The standard is then brought up to 100.0 mLs with methanol. 250 uLs of BNA Surrogate Spike Solution is added to all samples, method blanks (MBs), matrix spike/matrix spike duplicates (MS/MSDs) and laboratory control samples (LCS).

Compound	Concentration (ug/mL)
p-Terphenyl-d_4	100
Nitrobenzene-d_5	100
2-Fluorobiphenyl	100
1,2-Dichlorobenzene-d_4	100
Phenol-d_5	150
2-Fluorophenol	150
2,4,6-Tribromophenol	150
2-Chlorophenol-d_4	150

- Life of Standard: 6-months from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2

5.2.1.2 BNA Surrogate Spike (Low-Level 'Y' Matrix) Solution

The BNA Surrogate Spike ('Y' Matrix) Solution is prepared from the BNA Surrogate Spike at the levels listed below. 250 uLs of BNA Surrogate Spike Solution ('Y' Matrix) is added to all samples, MBs, LCSs and MS/MSD.

Compound	Concentration (ug/mL*)
p-Terphenyl-d_4	50
Nitrobenzene-d_5	50
2-Fluorobiphenyl	50
1,2-Dichlorobenzene-d_4	50
Phenol-d_5	75
2-Fluorophenol	75
2,4,6-Tribromophenol	75
2-Chlorophenol-d_4	75

*ug/mL = mg/L = ppm

- Life of Standard: 6-months from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2

5.2.1.3 Pesticide/PCB Surrogate Spike Solution

The surrogate used in the extraction of pesticides/PCBs from soil/sediments is a solution of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TCMX) in acetone at the concentrations listed below. 500 uLs of Pesticide/PCB Surrogate Spike Solution is added to all samples, MBs, MS/MSDs and LCS.

Compound	Concentration (ug/mL)
DCB	0.40
TCMX	0.40

- Life of Standard: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.1.4 PAH Surrogate Spike Solution

The surrogate used in the extraction of PAHs from soil/sediments is a solution of Decafluorobiphenyl and Benzo(e)pyrene in acetone at the concentrations listed below. The HPLC group prepares the working surrogate solution. 250 uLs of PAH Surrogate Spike Solution is added to all samples, MBs, MS/MSDs and LCS.

Compound	Concentration (ug/mL)
Decafluorobiphenyl	100
Benzo(e)pyrene	5.0

- Life of Standard: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.1.5 Diesel / DRO Surrogate

The surrogate used in the extraction of Diesel/DRO from soil/sediments is a solution of 2-Fluorobiphenyl and o-Terphenyl in acetone at the concentrations listed below. The Diesel/DRO analyst prepares the working surrogate solution. 250 uLs of Diesel/DRO Surrogate Spike Solution is added to all samples, MBs, MS/MSDs and LCS.

Compound	Concentration (ug/mL)
2-Fluorobiphenyl	200
o-Terphenyl	200

- Life of Standard: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.2 Laboratory Control Sample (LCS) & Matrix Spike (MS) Solutions

5.2.2.1 BNA TCL Spike Solution

The BNA TCL Spike Solution is prepared from two stock standards, 8270 LCS Mix and 3,3'-Dimethylbenzidine. See Attachments 4 and 5. 50.0 mLs of 8270 LCS Mix and 5.0 mLs of 3,3'-Dimethylbenzidine are pipetted into a 100.0 mL flask. Class A glassware must be used. The standard is then brought up to 100.0 mLs with methanol. 500 uLs of BNA TCL Spike Solution is added to the LCS and MS/MSD.

Compound	Concentration (ug/mL)
Acid Compounds	100
Base/Neutral Compounds	100

- Life of Standard: 6-months from the from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2.

5.2.2.2 BNA Matrix Spike (Low-Level 'Y' Matrix) Solution

The BNA Matrix Spike ('Y' Matrix) Solution is prepared from the BNA TCL Spike Solution found in Section 5.2.2.1. at the levels listed below. 500 uLs of BNA Matrix Spike ('Y' Matrix) Solution is added to the LCS and MS/MSD.

Compound	Concentration (ug/mL)
Acid Compounds	50
Base/Neutral Compounds	50

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

5.2.2.3 Pesticide (Full List) Spike Solution

The LCS/MS solution used in the extraction of pesticides or pesticides/PCB from soil/sediments is a solution of pesticides in methanol at the following concentrations. 500 uLs of Pesticide (Full List) Spike Solution is added to the LCS and MS/MSD.

Compound	Concentration
All compounds	0.40 ug/mL

- Life of Standard: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.2.4 PCB Spike Solution

The LCS/MS solution used in the extraction of PCBs from soil/sediments is a solution of Arochlor 1016 and Arochlor 1260 in methanol at the following concentrations. 500 uLs of PCB Spike Solution is added to the LCS and MS/MSD.

Compound	Concentration (ug/mL)
AR 1016	5.0
AR 1260	5.0

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

5.2.2.5 PAH Spike Solution

The LCS/MS solution used in the extraction of PAHs from soil/sediments is a solution of PAH compounds in acetonitrile at the following concentrations. The HPLC group prepares the spike solution. 250 uLs of PAH Spike Solution is added to the LCS and MS/MSD.

Compound	Concentration (ug/mL)
Acenaphthene	8
Acenaphthylene	16
Anthracene	0.8
Benzo(a)anthracene	0.8
Benzo(a)pyrene	0.8
Benzo(b)fluoranthene	1.6
Benzo(ghi)perylene	1.6
Benzo(k)fluoranthene	0.8
Chrysene	0.8
Dibenzo(a,h)anthracene	1.6
Fluorene	1.6
Indeno(1,2,3-cd)pyrene	0.8
Naphthalene	8
Phenanthrene	0.8
Pyrene	0.8

- Life of Standard: Same as the parent solution
- Storage Requirements: As stated in Section 5.2

5.2.2.6 Diesel / DRO

The LCS/MS solution used in the extraction of Diesel/DRO from soil/sediments is a solution of TEPH-DRO in methanol at the following concentration. The Diesel/DRO analyst prepares the spike solution. 250 uL of Diesel/DRO Spike Solution is added to LCS and MS/MSD.

Compound	Concentration
TEPH-DRO	4000.0 ug/mL

- Life of Standard: Same as the parent solution
- Storage Requirements: As stated in Section 5.2

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control

The following QC is performed with each organic extraction batch. An extraction batch contains samples of similar matrix that are logged in for the same test code. An extraction batch may contain no more than 20 samples.

7.1.1 Method Blank (MB)

The MB is heat purified powdered sodium sulfate, which has been spiked with the appropriate surrogate compound(s) (Sec. 5.2.1), taken through the entire extraction procedure, and is used to monitor the introduction of artifacts into the process. This demonstrates that the materials used are free of interferences.

7.1.2 Laboratory Control Sample (LCS)

The LCS is heat purified powdered sodium sulfate which has been spiked with a predetermined quantity of spike solution (Sec. 5.2.2) with the appropriate analytes of interest and the appropriate surrogate solution (Sec. 5.2.1).

7.1.3 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

In MS/MSD analysis, predetermined quantities of spike solutions of specified analytes (Sec. 5.2.2) and surrogate (Sec. 5.2.1) are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected by the analysis. The relative percent difference between the samples is calculated and used to assess analytical precision.

7.1.4 Surrogate

A surrogate is an organic compound(s) which is similar to the analytes of interest in chemical composition, extraction and chromatography, but which is not normally found in environmental samples. Surrogate(s) are added to **all** MBs, MS/MSDs, LCSs, and samples prior to extraction and analysis. Percent recoveries are calculated for each surrogate.

7.2 Sample Collection, Preservation and Handling

Sample container, preservation technique and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract/client requests. In general, samples collected for soil/sediment extractions are collected in 8 oz. wide-mouth glass jars, with Teflon-lined screw-cap lids. If a Teflon-lined lid is not available, solvent-rinsed aluminum foil can be used as a liner.

Samples, sample extracts and standards are stored separately.

NOTE: If the sample matrix is highly acidic or basic, corrosion of the foil may occur and contaminate the sample.

Samples are stored at 4 ± 2°C prior to extraction. Any samples received by the preparation group that do not comply must be noted. Deviations in results "could" be explained by the failure of sample collector/client/custodian to comply to sample collection and storage requirements.

Matrix	Holding Time (vts)
Soils / Wastes	14 days

vts = verified time of sample collection

7.3 Sample Preparation

7.3.1 Glassware Preparation

7.3.1.1 All glassware (except Snyder columns, volumetric flasks, volumetric pipets, and syringes) must be washed thoroughly with warm soapy water, rinsed **5**-times with hot tap water and rinsed **3**-times with DI water. The stopcocks of the separatory funnels should be cleaned with a small brush. **It is absolutely mandatory that all glassware be scrupulously clean.** Failure to rinse well with water, may leave a soap film that is incompletely removed with solvent rinsing, and with subsequent extraction, "soap" peaks will appear in the chromatograms.

7.3.1.2 If glassware is very wet, it may be towel dried. **All** Glassware should be rinsed with acetone, and the excess should be discarded into the appropriate waste container. This step is done to ensure that the glassware is dry. **If after rinsing once, the glassware still contains any water, repeat the acetone rinse.** At this point, let the

glassware dry before continuing to ensure that all of the water is gone. All glassware should then be rinsed with DCM using a Teflon squeeze bottle, and the excess discarded into the appropriate waste container. Repeat this step at least **3**-times and allow the glassware to dry. Failure to remove all water prior to DCM rinsing prevents the DCM solvent from coming into contact with all surfaces on the glassware. The solvent rinse is then incomplete, and may leave contaminants on the glass, which are then co-extracted with the sample.

NOTE: DCM is considered a health hazard. It is harmful if swallowed or inhaled. The vapor is irritating and thus should be used in a hood. It is readily absorbed through the skin and contact may be irritating.

7.3.2 Procedures for Return of Glassware to Dishroom

Any glassware that has organic residue present, all K-D receivers, and all separatory funnels should be rinsed with acetone, or whatever other solvent which removes the residue, prior to return to the dishroom from the lab. Glassware in which the residue can not be removed should be segregated from other glassware being returned to the dishroom. Glassware should be carefully placed in a tub and placed on the "Dirty" side of the dish racks. In order to reduce glassware breakage, glassware should not be stacked in the tubs. Severely chipped glassware should be removed from service. Some items are repairable. Check with the supervisor as to what items get repaired.

7.4 Calibration/Standardization

Not Applicable.

7.5 Preventive Maintenance

- Balance must be cleaned and checked for levelness prior to each use. Class "S" weights must be weighed and documented each day the balance is used. Consult your supervisor if the weights are out of acceptable limits. Do not use the balance until the situation is back in control.
- The N-Evap water bath should also contain DI water. The water level in the bath should be sufficient to cover 3/4 of the receivers when submerged.
- The thermometer used in the extraction water baths are checked against a reference NIST thermometer on a yearly basis or sooner if necessary.
- The desiccant used in the desiccator should be removed and dried in an oven at 130°C whenever the color indicates that it is saturated with moisture. This is usually indicated by a change of color from blue to purple/pink.
- To avoid the breakage of sample extracts, the analyst needs to take care that the containers are properly balanced on the centrifuge. The container should fit snugly in the holder. Use a paper towel to cushion the centrifuge bottles if necessary.

7.6 Sample Analysis

7.6.1 Analytical (Preparation) Sequence

The following preparation sequence will be required of each extraction batch of at most, 20 samples:

Quality Control	Frequency
MB	1 per extraction batch of at most 20 samples
LCS [1]	1 set per extraction batch of at most 20 samples
MS/MSD[2]	At least 1 set in 20 samples (may be requested by the client)
Surrogate	Every sample / MB / LCS / LCD / MS / MSD

[1] An LCS Duplicate (LCD) is performed in insufficient sample is available for an MS/MSD.
[2] The sample selection for MS/MSD, if not specified by the client on the chain-of-custody, is rotated among client samples so that various matrix problems may be noted and/or addressed.

7.6.2 Extraction Process

NOTE: All soils and sediments receive total solids analysis on them by the metals department, so the extraction analyst should not have to perform this step. Results are available on LIMS.

7.6.2.1 Sample Homogenization

Prepare the mixing pan by completely covering the inside with aluminum foil. The dull side of the foil should be toward the sample. Complete the following steps as quickly as possible so as to avoid losses of the more volatile extractables. Transfer the entire contents of the sample container to the mixing pan. Mix the sample well. Using a wooden spatula or solvent-rinsed, stainless steel spatula, break up any chunks of soil material. The objective is to get as representative of a sample as possible. If objects such as rocks and plant material seem "foreign", they should not be used for the sample. However, sometimes material other than soil constitutes a large portion of the sample. These materials should be represented in the sample.

NOTE: If a soil or sediment sample contains more than 90% moisture, it is generally extracted using the separatory funnel method. Contact your supervisor immediately in this case.

7.6.2.2 Sample Preparation

pH Determination (optional)
Weigh out the pH sample aliquot at the time as the extraction aliquot is weighed out. Weigh out 50 grams of sample into a 250 mL beaker for pH determination. Add 50 mLs of deionized water. Add a Teflon-coated stir bar and cover tightly with aluminum foil. Stir for one hour on a magnetic stir plate. Determine the pH of the sample with wide range pH paper. Record the pH value in the extraction logbook. If the pH of the sample is <5 or >11, notify your supervisor. If sample is limited, use 5 grams of soil and 5 mLs of reagent water for pH determination. Note this in the extraction log. Solid and liquid waste from pH determination should be placed in appropriate waste containers. No pH waste is to be put in the sink.

7.6.2.2.1 Weigh a 15 gram (record to nearest 0.01 gram) sample into a 100 mL beaker. Add powdered, sodium sulfate to the sample and stir with disposable wooden spatula. Add sodium sulfate until the sample has a "free-flowing" consistency.

7.6.2.2.2 Plug a glass extraction thimble with a small amount of soxhlet-extracted glass wool. (Alternately, 70 mm Whatman 541 filter paper can be used in place of glass wool.) Add a sufficient amount of granular sodium sulfate to the bottom of the thimble. This aids in drying the extract as it flows through the thimble and into the beaker. Transfer the dried sample to the glass extraction thimble. Place a thimble support around the extraction thimble. Set the extraction thimble into an extraction beaker. The MB an LCS will consist of 15 grams of granular sodium sulfate. Prepare blanks in the same manner as samples.

7.6.2.2.3 Add the appropriate amount of surrogate spike solution to every sample, MB, LCS and MS/MSD.

7.6.2.2.4 Add appropriate amount of spike solution to the LCS and MS/MSDs.

7.6.2.2.5 The solvent used for Pesticides, and PCBs hexane:acetone (1:1). The solvent used for BNAs, PAHs, and Diesel/DRO is DCM:Acetone (1:1).

7.6.2.2.6 Add a couple Teflon boiling chips to each extraction beaker. Carefully add 120 mLs* of extraction solvent to the extraction beaker. The sample contained in the extraction thimble should now be submerged in the extraction solvent.

***NOTE:** More solvent may be added to ensure that the sample is fully immersed. For the MB and LCS/LCSDs less solvent is added; add 110 mLs when the DCM:acetone solvent is used and 115 mLs when the hexane:acetone is used.

7.6.2.3 The Soxtherm Automated Soxhlet Extraction Unit

7.6.2.3.1 Check the waste solvent tank and empty if necessary.

7.6.2.3.2 Verify that the nitrogen regulator is set at 65 PSI and that there is sufficient nitrogen supply.

7.6.2.3.3 Verify sufficient water pressure is supplied to the unit.

7.6.2.3.4 Program the Soxtherm unit using the following parameters.

Parameter	Entered Value
Temperature Cutoff	200°C
Extraction Temperature	150°C (DCM:Acetone 1:1) 160°C (Hexane:Acetone 1:1)
Boiling Time	0 hrs. 55 min.
Solvent Reduction A	4 X 15 mL
Extraction Time	0 hrs. 55 min.
Solvent Reduction B	2 X 15 mL
Solvent Cooling Time	0 hrs. 10 min.
Solvent Reduction Interval	5 min
Solvent Reduction Pulse	5 sec.
Total Program Time	calculated by unit

7.6.2.3.5 For sample loading, the condensers of the Soxtherm should be in their raised position. Wipe down the Teflon extraction cylinder with DCM to prevent contamination from previous samples. Install the extraction beakers into position on the unit. Center the extraction beaker over the aluminum heating block. The Teflon extraction cylinder makes a seal with the extraction beaker, so the beaker must not have any chips.

7.6.2.3.6 Press the ENTER button to start the run. The Soxtherm Automated Soxhlet Extraction Unit should operate unattended. No operator intervention is required until the second solvent reduction (~2 hours).

7.6.2.3.7 "Boiling Time" is the time selected in which the system is in total reflux with the sample immersed in boiling solvent. After the programmed 55 minutes, the system enters "Solvent Reduction A" phase. The system is not in reflux. The condensate is collected in the 15 mL reservoir cups and a pulse of nitrogen transfers the aliquot to the waste tank. Performing this step 4 times removes 60 mLs of the extraction solvent. The extraction solvent level in the extraction beaker should now be below the extraction thimble.

7.6.2.3.8 "Extraction Time" is the selected time in which the solvent is boiled and the condensed solvent runs through the sample in the thimble and drips out into the extract below. The system is in total reflux again during this phase.

7.6.2.3.9 The next phase is "Solvent Reduction B" which again traps and removes 15 mLs aliquots of condensed solvent. This is the point where operator intervention may be needed. The system is programmed to perform two solvent reductions in this phase which will result in 30 mLs of extraction solvent being removed from the system. "Solvent Reduction A" phase removes 60 mLs. A total of 110 mLs of solvent will be removed from the system. Theoretically, 10 mLs of extraction solvent should be left in the extraction beaker (120 initial volume - 110 mL removed by solvent reduction = 10 mL). Due to instrument limitations, this is not always the case. The operator has to **carefully monitor this reduction step** and remove an extraction beaker if the extract volume becomes too low. **NOTE:** For samples using the DCM:acetone(1:1) solvent system place the metal cooling grid beneath the beaker when the remaining solvent reaches the appropriate volume. This ensures that the extract cools while still attached to the condenser.

If an extraction beaker has to be removed, raise the condensers and use tongs to remove the extraction beaker. Lower the condensers and proceed with the solvent reduction on the remaining samples.

7.6.2.3.10 After the solvent reduction, the system enters "Solvent Cooling Time". During this time, the heating blocks are no longer heating; however, the solvent may still boil. For this reason, the sample extracts have to be monitored closely and removed if the solvent volume becomes to low.

7.6.2.3.11 After the extract cools, transfer it to a 16X125 test tube through a small funnel containing granular sodium sulfate. The test tube should be marked with the appropriate final volume. Rinse the extraction beaker with a small amount of hexane (for pesticides and PCBs) or DCM (for BNAs, PAHs, and DROs or samples to be loaded on the GPC) and transfer that rinse to the test tube. Repeat the rinse 2-more times.

7.6.2.4 Sample Concentration

7.6.2.4.1 Nitrogen Evaporation

7.6.2.4.1.1 For further concentration, place each receiver or test tube on the N-Evap tray. The N-Evap outlet needles should be stored in a 600 mL beaker containing DCM:Acetone (1:1) mixture prior to each use. Wipe each outlet needle with a DCM soaked KimWipe and lock into place on the N-Evap. Lower the outlet tube into the receiver being careful not to touch the sides of the receiver. The outlet tube should remain above the surface of the extract. Open the valve of the nitrogen tank and adjust the pressure in order to achieve the appropriate nitrogen stream. The nitrogen stream should make a slight "dimple" in the surface of the extract. If the extract bubbles, the nitrogen stream is **not** gentle enough. Lower the entire N-Evap tray into the warm water bath to aid the evaporation process. Heat is not necessary and if used the temperature should not exceed 35°C.

7.6.2.4.1.2 Some soil extracts contain sediment after concentrating on the water bath. If this is the case, the extraction analyst will transfer the sample extract (including the sediment) from the receiver to a screw-top test tube. The sample extract is centrifuged and the supernatant is transferred back to the appropriate receiver. The residue that is left in the screw top test tube is washed with 1 mL of appropriate solvent (see corresponding test instructions below for final solvent) and centrifuged. The "wash" supernatant is added to the appropriate receiver and the sample is placed on the Nitrogen evaporator to be concentrated. All samples requiring this centrifuging step are documented in the logbook.

7.6.2.4.1.3 The extracts must never be allowed to go dry. While the extracts are concentrating, occasionally rinse down the sides of the receiver or test tube with appropriate solvent (see corresponding test instructions below).

7.6.2.4.1.4 Refer to appropriate test below for further concentration instructions:

BNAs

a. Once the extracts reach ~1 mLs, remove from the N-Evap. Label a 1.5-2 mL screw capped vial with appropriate sample number. Transfer the ~1 mLs to the vial using a transfer pipet. Rinse the test tube with a little (< 1/4 mL) DCM and add to the vial. Rinse the test tube with a little more DCM (< 1/4 mL). Transfer to sample vial. Bring up the sample volume (if necessary) to ~1 mL with another DCM rinsate. The extraction analyst must rinse the test tube at least two times. The use of a 500 uL syringe gives the analyst more control when adding the small-volume DCM rinses to the receiver. If the rinsates make the extract more than the 0.5 mLs, the analyst may hold the vial under the stream of nitrogen momentarily to reduce the volume back down to 1.0 mLs. The GC/MS analyst will bring the sample extract to exactly 0.5 mLs prior to analysis. Seal vial with a Teflon-lined screw-cap.

b. There will be samples that will not concentrate to a 0.5 mL final volume. In these cases, bring the sample up to the smallest final volume (increments of 1 mL)* that the sample and three rinses will transfer into. All changes in final volume must be documented in the extraction logbook. Notify your supervisor.

* Volumetrically add the appropriate volume of DCM to a 16X125 screw top test tube and mark the meniscus using a fine-tipped marker. Discard the DCM into an appropriate waste vessel. Bring up the sample to volume using this test tube.

c. All samples pertaining to one extraction batch are placed in a plastic vial holder and secured. A listing of the entire contents of the batch, including clients, sample numbers, batch number and standard numbers, is to be placed **WITH** the set. To relinquish samples, the extraction analyst takes the sample extracts and the extraction logbook to the sample extract refrigerator (located in the GC/MS Lab).

d. An analyst from the GC/MS BNA group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction logbook. All extracts are to be kept at 4±2°C in the dark, until analysis.

PCBs, Pesticide/PCB (No GPC Cleanup)

a. Concentrate the sample to the about 1 mL to remove excess Acetone. Bring up to 5.0 mLs with hexane.

(***PCBs** - refer to the mandatory sulfur acid cleanup in SOP No. USP-003.)

b. All samples pertaining to one extraction batch are placed in a test tube rack. Each test tube should have the extraction batch number, sample numbers, and test code written on it.

c. To relinquish samples, the extraction analyst takes the sample extracts and the extraction logbook to the sample cooler area (located in the GC extractables lab). An analyst from the GC extractables group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction logbook. All extracts are to be kept at 4 ± 2°C in the dark, until analysis.

PCBs, Pesticide/PCB (With GPC Cleanup)

a. Concentrate the sample to the about 1 mL to remove excess Acetone. Bring up to 10.0 mLs with DCM.

Refer to USP-SOP-003 Cleanup Procedures for GC & GC/MS Extracts.

PAHs

a. Concentrate the sample to ~1 mL to remove any remaining DCM:Acetone. Dilute the sample up to 5.0 mLs with acetonitrile. Blow back down to ~1 mL and bring up to 2.5 mLs with acetonitrile.

b. All samples pertaining to one extraction batch are placed in a test tube rack. Each test tube should have the extraction batch number, sample number, and test code written on it.

c. To relinquish samples, the extraction analyst takes the sample extracts and the extraction logbook to the sample cooler area (located in the GC extractables lab). An analyst from the HPLC group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction logbook. All extracts are to be kept at 4 ± 2°C in the dark, until analysis.

7.6.2.4.1.5 In some soil samples with large amounts of oils, tars, or other methylene chloride/acetone extractables, the volume of the extract will be 100 mLs. Use a 100 mL volumetric flask to dilute the final volume to 100 mLs of acetonitrile.

7.6.2.4.1.6 The analyst who is performing the sample concentration needs to be aware which samples are going to receive further cleanup so the appropriate concentration steps are taken. More details may be found in Sample Extract Cleanup SOP (USP-003).

7.6.2.5 Screening and Cleanup

Samples are not pre-screened prior to extraction. Unless previous experience has proven high concentrations and/or background a 15 gram sample will be extracted. In those cases where deemed appropriate, a 1 gram portion may be taken for extraction.

If samples are known to have extremely high concentrations of pesticides/PCB or background material, alternate glassware may be used, including glass funnels instead of Buchner funnels. Buchner funnels have areas that are very difficult to clean.

Sludge samples are a mixture of water and suspended solid materials. If the percent moisture of a given sludge is known to be greater than 90%, a 15 gram or 30 gram portion may be weighed and added to 1000 mLs of reagent water. It is then extracted like a water matrix as described in SOP No. USP-3520, Continuous Liquid-Liquid Extraction Procedure. They are not extracted by the soxhlet method.

It is not mandatory that samples be subjected to further cleanup steps prior to analysis. If it is determined that the sample set needs a GPC cleanup or a florisil cleanup refer to the appropriate section of USP-003.

7.7 Documentation

All extraction information must be carefully documented in the appropriate extraction log (Attachment 1). This includes any additional sample or extraction information; and problems and/or deviations from normal procedure. The supervisor should be notified and a Sample Discrepancy Report (SDR) or Non-Conformance Memo (NCM) may need to be initiated.

An extraction batch contains samples of similar matrix that are logged in for the same test code.

An extraction batch may contain different analyte list identifiers. The test method for BNAs is 3541BN; Pesticides is 3541CP; PCBs is 3541PC; Diesel/DRO is 3541D; and PAHs is 3541PN.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 At least one MB and LCS will be included in each laboratory batch of 20 samples. The MBs will be examined to determine if contamination is being introduced in the laboratory. The LCS will be examined to determine both precision and accuracy.

8.1.2 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

8.1.3 Precision will be measured by the reproducibility of the LCS between batches and can be calculated as Relative Percent Difference (RPD). Results must agree within statistical control limits in order to be considered acceptable.

8.1.4 The MS/MSD monitor the effect of sample matrix on method precision and accuracy, but are not used to determine if reanalysis is required.

8.1.5 Surrogate compounds will be added to every sample to measure performance of the analysis. Results must agree within statistical control limits in order to be considered acceptable.

8.2 Corrective Actions

The extraction analyst must perform the Quality Control described in Section 8.1. The extraction analysts will not know if all QC is in control until the analysis of the batch is completed. It is the responsibility of the GC extractables, HPLC and GC/MS labs to inform the Organic Extractions Department (by initiating an Sample Discrepancy Report - SDR or Non-Conformance Memo - NCM) when a sample or set of samples requires re-extraction. Re-extractions are to be designated as R1 in the extraction process.

All problems and/or deviations from normal procedures must be documented in the extraction log. The supervisor should be notified and a SDR or NCM may need to be initiated.

9.0 Data Analysis and Calculations

Not Applicable.

10.0 Waste Management and Pollution Control

The following waste streams are produced when this method is carried out.

- Waste chlorinated solvents produced by this method are line fed from the Sox-Therm to the Waste Chlorinated Solvent carboys located below the Sox-Therm table.
- Remaining soil samples produced by this method shall be disposed of into the Non-Hazardous Waste solids containers.
- Any unused extracts remaining from this method shall be turned over to the EHSC to be collected for disposal.

11.0 Method Performance Criteria

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

Attachment 1: Example: Extraction Log
Attachment 2: Example: Extraction Flowcharts.
Attachment 3: BNA Surrogate Stock Solution
Attachment 4: 8270 LCS Mix
Attachment 5: 3,3'-Dimethylbenzidine

Historical File:

	Revision 00: 06/14/99		Revision 05: 08/16/06
	Revision 01: 09/14/00		
	Revision 02: 08/16/03		
	Revision 03: 10/24/03		
	Revision 04: 01/31/05		

Reasons for Change, Revision 05:

- Annual Review.
- Remove Organophosphorus Pesticides.
- Add 541 filter paper to section 7.6.2.2.2.
- Add JP4 and JP8 Appendix.
- Add AR242 and AR1254 Appendix.
- Section 8.1 - Added reference to the Non-Conformance Memo (NCM)

U:\QC\SOP\USP-3541.DOC

Attachment 1.

Example: Extraction Log

Extraction Date:_____ STL Chicago Page No.:_____
Method Code:_____ Organic Extraction Record Batch No.:_____
Solvent:_____ GC/MS Semi-Volatiles Analyst Initials:_____
Solvent Lot No.:_____ Balance ID No.:_____
Solvent Dispenser Volume Checked:_____
Acid / Base (circle & define):_____ Lot No.:_____ Sodium Sulfate Lot No.:_____

Matrix:
a. Water
b. Soil
c. Other_____

Extraction Method:
a. SW-846 3510 (Sep Funnel)
b. SW-846 3550 (Sonication)
c. SW-846 3580 (Waste Dil.)
d. SW-846 3520 (Cont.)
e. SW-846 3541 (Soxhlet)
f. Other:_____

Method Extraction Times:
Start Time:_____
End Time:_____

	Sample #	Sample ID	ICOC	pH[1]	Initial Vol/Wt. (mLs/g)	Final Vol.[2] (mLs)	K-D'd (√)	Clean-Up Absorbent	Multipliers		
									Surr.	Spike	Split
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											
21											
22											
23											
24											
25											

[1]Sample pH / Acid Adjusted pH / Base Adjusted pH
[2]The extract volume for BNAs is ~0.8 mLs when the final volume is documented as 1.0 mL. Final volume adjustment is completed in the BNA dept.

___ Insufficient Sample for MS/MSD ___ MS/MSD Not Requested (Limited Vol.) ___ MS/MSD Designated ___MS/MSD Chosen
___ Sample Container Shake ___ Sample Container Shaken & Rinsed with Solvent ___ Sample Container Not Shaken Due To:____

Comments/Variance:_____

Surrogate:_____ Volume:_____ Std. ID#:_____
LCS/MS Solution:_____ Volume:_____ Std. ID#:_____
LCS/MS Solution:_____ Volume:_____ Std. ID#:_____

Analyst Signature:_____ Date:_____
Reviewer Signature:_____ Date:_____

Extraction Custody Record

Extracts Transferred	Relinquished by	Date	Time	Received by	Date	Time	Reason for Transfer

Analysis Custody Record

Sample(s)	Date/Time Out	Date/Time In	Analyst	Sample(s)	Date/Time Out	Date/Time In	Analyst

Extraction Date:_____ STL Chicago Page No.:_____
Method Code:_____ Organic Extraction Record Batch No.:_____
Solvent:_____ GC Extractables/HPLC Analyst Initials:_____
Solvent Lot No.:_____ Balance ID No.:_____
Solvent Dispenser Volume Checked:_____
Acid / Base (circle & define):_____ Lot No.:_____ Sodium Sulfate Lot No.:_____

Matrix:
a. Water
b. Soil
c. Other_____

Extraction Method:
a. SW-846 3510 (Sep Funnel)
b. SW-846 3550 (Sonication)
c. SW-846 3580 (Waste Dil.)
d. SW-846 3520 (Cont.)
e. SW-846 3541 (Soxhlet)
f. Other_____

Method Extraction Times:
Start Time:_____
End Time:_____

	Sample #	Sample ID	ICOC	pH	Initial Vol/Wt. (mLs/g)	Final Vol.[1] (mLs)	K-D'd (√)	Clean-Up Absorbent	Multipliers		
									Surr.	Spike	Split
1											
2											
3											
4											
5											
6											
7											
8											
9											
10											
11											
12											
13											
14											
15											
16											
17											
18											
19											
20											
21											
22											
23											
24											
25											
26											
27											

[1]The extract volume is ~2.0 mL for Herbicides and 10 mL for TCLP Pesticides. The final volume documented for these extracts, 10 mLs and 100 mLs respectively, reflects the adjusted measures prepared by the instrumentation analysts.

___ Insufficient Sample for MS/MSD ___ MS/MSD Not Requested (Limited Vol.) ___ MS/MSD Designated ___MS/MSD Chosen
___ Sample Container Shaken ___ Sample Container Shaken & Rinsed with Solvent ___ Sample Container Not Shaken Due To:_____

Comments:_____

Surrogate:_____ Volume:_____ Std. ID#:_____
LCS/MS Solution:_____ Volume:_____ Std. ID#:_____
LCS/MS Solution:_____ Volume:_____ Std. ID#:_____

Analyst Signature:_____ Date:_____
Reviewer Signature:_____ Date:_____

Extraction Custody Record

Extracts Transferred	Relinquished by	Date	Time	Received by	Date	Time	Reason for Transfer

Analysis Custody Record

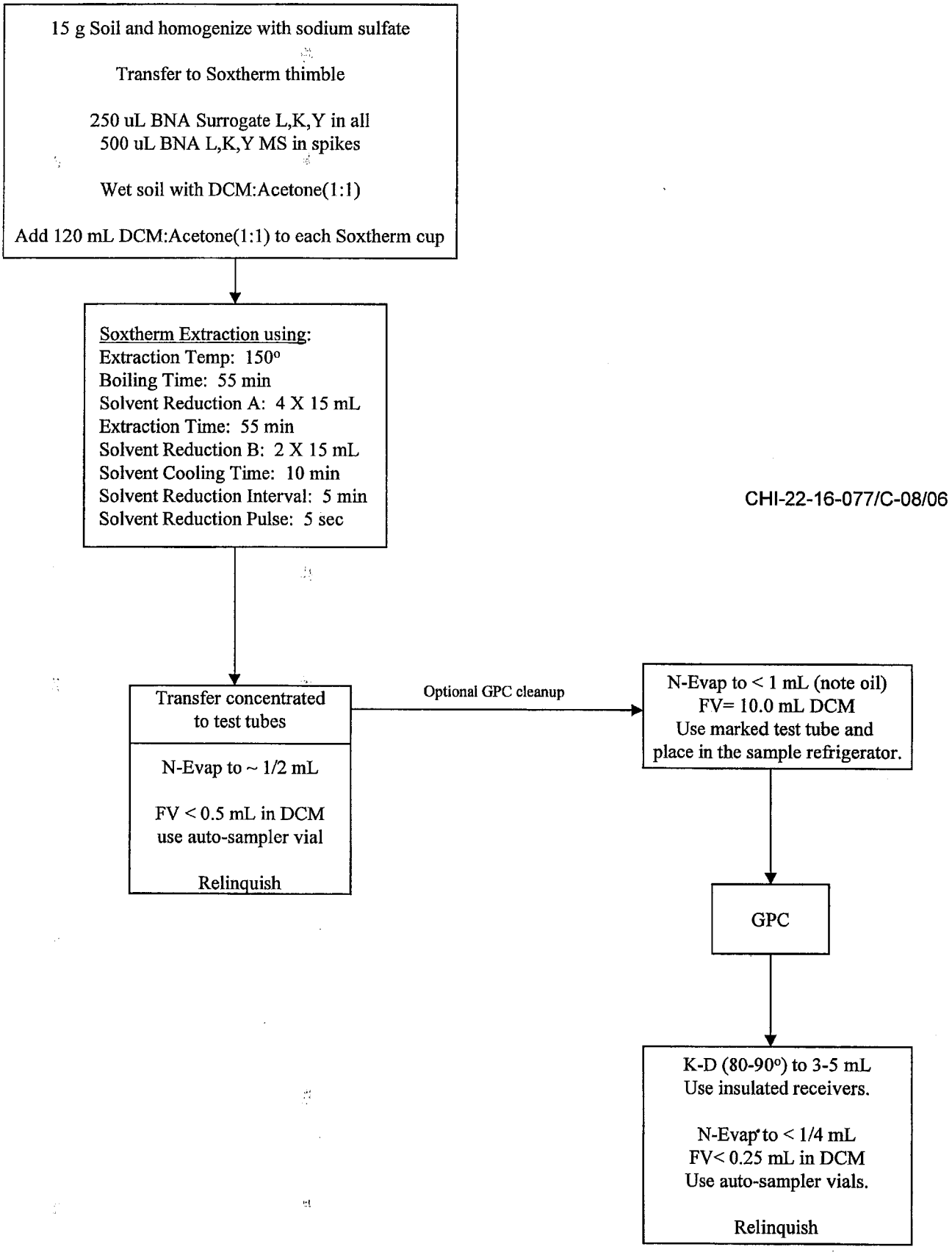
Sample(s)	Date/Time Out	Date/Time In	Analyst	Sample(s)	Date/Time Out	Date/Time In	Analyst

24 A thru F

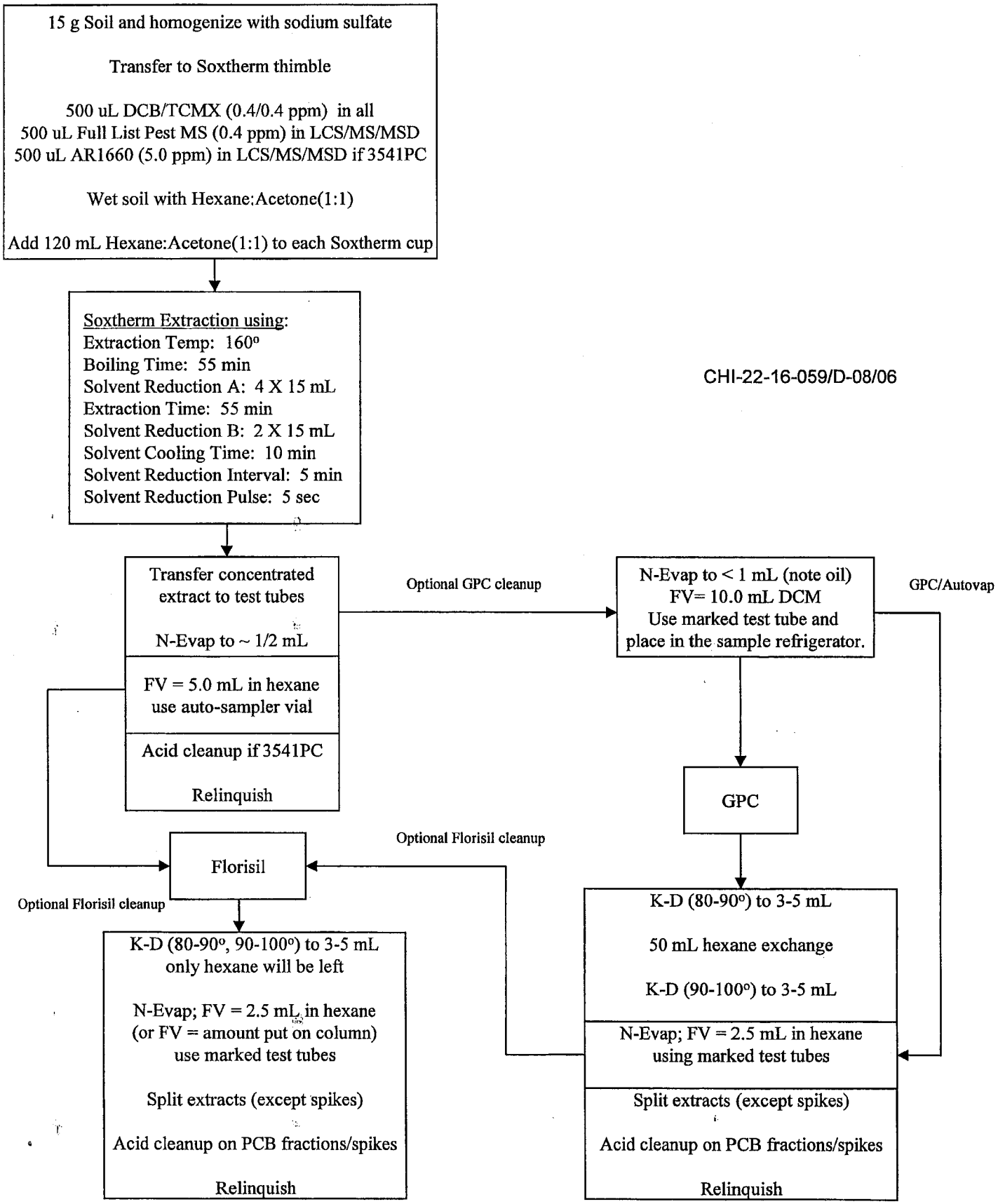
Attachment 2.

Example: Extraction Flowcharts

Flowchart for BNA Soil (8270)
by 3541
3541BN



Flowchart for Pesticide/PCB Soil (8081, 8082)
by 3541
3541CP, 3541PC, HYDPPS



24B

Flowchart for PAH Soil (8310)
by 3541
3541PN

15 g Soil and homogenize with sodium sulfate

Transfer to Soxtherm thimble

250 uL PAH Surrogate (DFB/BEP) in all
250 uL PAH Full List MS in spikes

Wet soil with DCM:Acetone(1:1)

Add 120 mL DCM:Acetone(1:1) to each Soxtherm cup

↓

Soxtherm Extraction using:
Extraction Temp: 150°
Boiling Time: 55 min
Solvent Reduction A: 4 X 15 mL
Extraction Time: 55 min
Solvent Reduction B: 2 X 15 mL
Solvent Cooling Time: 10 min
Solvent Reduction Interval: 5 min
Solvent Reduction Pulse: 5 sec

↓

Transfer concentrated extract
to 2.5 mL marked test tubes

N-Evap to < 1/2 mL

2 mL Acetonitrile exchange

N-Evap to < 1/2 mL

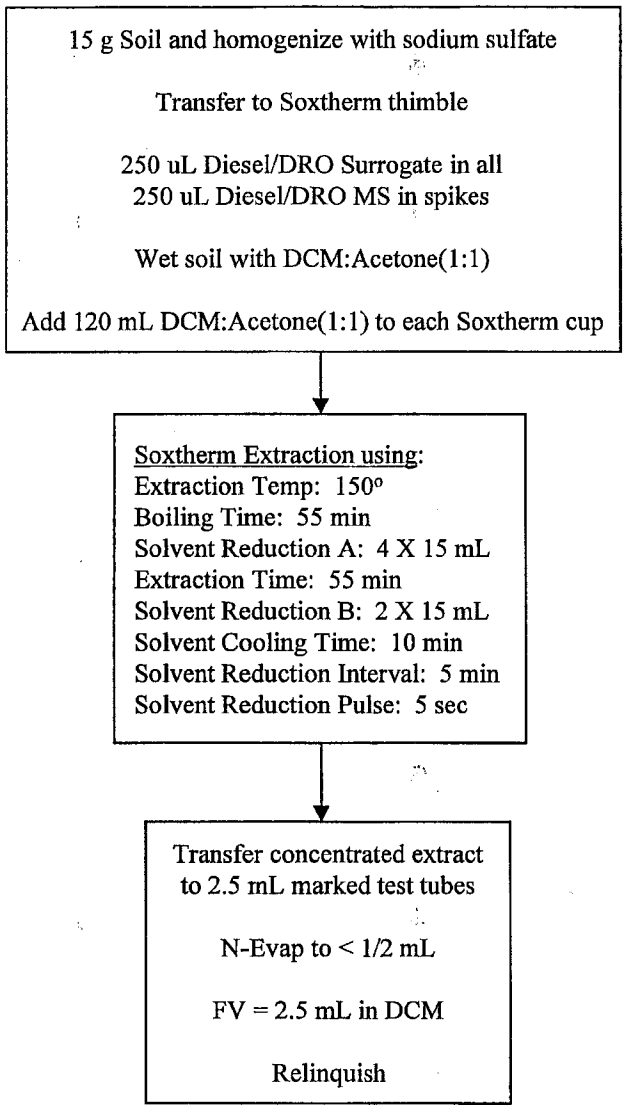
FV = 2.5 mL in Acetonitrile

Relinquish

CHI-22-16-060/D-08/06

24 C

Flowchart for Diesel/DRO Soil
by 3541
3541D



CHI-22-16-078/C-08/06

Flowchart for Jet Fuel in Soil
by 3541
3541J4, 3541J8

15 g Soil and homogenize with sodium sulfate

Transfer to Soxtherm thimble

250 uL Diesel/DRO Surrogate in all
250 uL J4 MS in spikes
Or
250 uL J8 MS in spikes

Wet soil with DCM

Add 120 mL DCM to each Soxtherm cup

↓

Soxtherm Extraction using:
Extraction Temp: 150°
Boiling Time: 55 min
Solvent Reduction A: 4 X 15 mL
Extraction Time: 55 min
Solvent Reduction B: 2 X 15 mL
Solvent Cooling Time: 10 min
Solvent Reduction Interval: 5 min
Solvent Reduction Pulse: 5 sec

↓

Transfer concentrated extract
to 2.5 mL marked test tubes

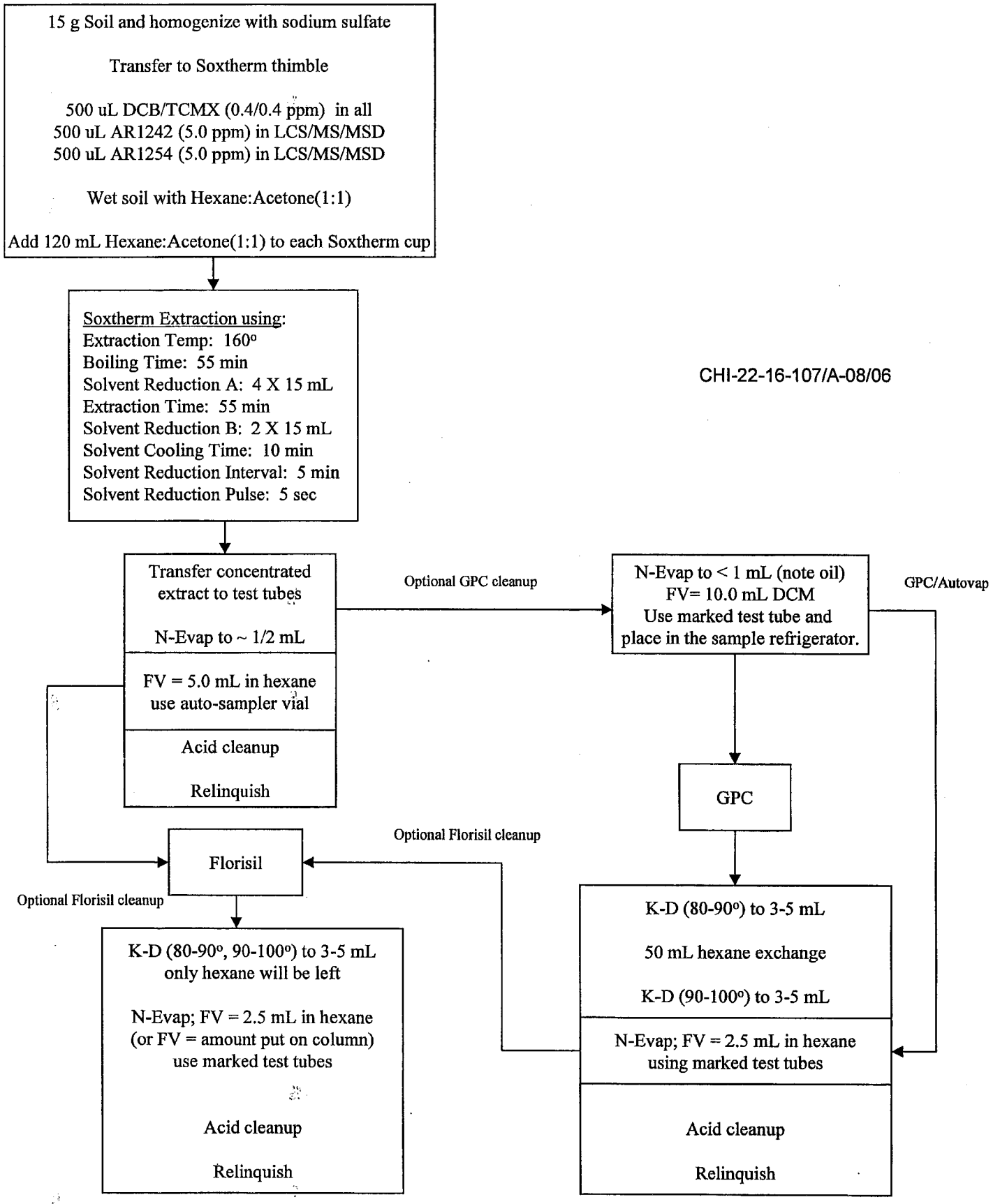
N-Evap to 2.5 mL

FV = 2.5 mL in DCM

Relinquish

CHI-22-16-106/A-08/06

Flowchart for AR1242, AR1254 Soil (8082)
by 3541
3541SH



Attachment 3.

Example: BNA Surrogate Stock Solution

Certificate of Composition

EX BNASUP ...8

0606SBNAA

DESCRIPTION: Semi-Volatile Acid/Base Surrogate Spike (High)

CATALOG NO.: 861142 MFG DATE: Nov-2005

LOT NO.: LB34829 EXPIRATION DATE: Nov-2008

Rec: 07/24/06

STC EXP: 07/24/07

SOLVENT: METHYLENE CHLORIDE

ANALYTE (1)	CAS NUMBER	PERCENT PURITY (2)	WEIGHT CONCENTRATION (3)	SUPELCO LOT NO
NITROBENZENE-D5	4165-60-0	99.9	1000	LB29556
P-TERPHENYL-D14	1718-51-0	99.9	1000	LB31973
PHENOL-D6	13127-88-3	99.9	1500	LB23082
1,2-DICHLOROBENZENE-D4	2199-69-1	99.9	1000	LB24284
2-CHLOROPHENOL D4	93951-73-6	98.6	1500	LB12871
2-FLUOROBIPHENYL	321-60-8	99.9	1000	LB12824
2-FLUOROPHENOL	367-12-4	99.7	1500	LB08773
2,4,6-TRIBROMOPHENOL	118-79-6	99.9	1500	LB21400

(1) Listed in alphabetical order.

(2) Determined by capillary GC-FID, unless otherwise noted.

(3) NIST traceable weights are used to verify balance calibration with the preparation of each lot. Concentration of analyte in solution is ug/ml +/- 0.5%, uncertainty based upon balance and Class A volumetric glassware. Weights are corrected for analytes less than 98% pure.

Elwood Doughty

Elwood Doughty
QA Manager

Supelco warrants that its products conform to the information contained in this publication. Purchaser must determine the suitability of the product for its particular use. Please see the latest catalog or order invoice and packing slip for additional terms and conditions of sale.

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26A thru 26D

Attachment 4.

Example: 8270 LCS Mix

Cerilliant™
Science. Down to a science.™

ERS-077
ER070605-01
Revision 1

Certificate of Analysis

EXBNASPP...13

0606LMPCA

8270 LCS Mix

Rec: 07/24/06
STL EXP: 07/24/07

Catalog Number:	ERS-077
Solution Lot:	ER070605-01
Expiration Date:	July 2008
Solvent:	Acetone::Methylene chloride (48::52)
Amount per Ampule:	5 mL
Storage:	Protect from light, store in freezer.
Handling:	We advise laboratories to use measured volumes of this standard solution before diluting to the desired concentration.
Intended Use:	For laboratory use only. This product is a quantitative standard useful for calibration, quality control, and other general applications requiring accurate solutions.

* *All analyte data can be found on the following pages.*

Cerilliant certifies that this standard meets or exceeds the specifications stated in this data sheet. Accuracy is ensured by exhaustive purity determinations and gravimetric preparation using balances calibrated with NIST traceable weights. Precision is guaranteed by triplicate analysis and comparison to previous lots (when available). Finally, homogeneity is demonstrated by random analysis of the ampuled standard.

Authorized Signature: Lara Sparks

Lara Sparks, Quality Assurance Director

August 18, 2005

Date

Component	Lot Number	Purity[1]	Concentration
Acenaphthene	29697-41	99%	200.0 µg/mL
Acenaphthylene	34267-35	99%	200.0 µg/mL
Acetophenone	EB-1807	99%	200.0 µg/mL
Aniline[2]	EB-1265	99%	200.0 µg/mL
Anthracene	34704-77	99%	200.0 µg/mL
Azobenzene	EB-1765	99%	200.0 µg/mL
Benz(a)anthracene	34764-06	99%	200.0 µg/mL
Benzidine[2]	EB-2071	99%	200.0 µg/mL
Benzo(b)fluoranthene	33385-53	99%	200.0 µg/mL
Benzo(k)fluoranthene	34750-27	99%	200.0 µg/mL
Benzo(g,h,i)perylene	34750-40	99%	200.0 µg/mL
Benzo(a)pyrene	34764-10	98%	200.0 µg/mL
Benzoic acid	EB-1162	99%	200.0 µg/mL
Benzyl alcohol	EB-0624	99%	200.0 µg/mL
Biphenyl	EB-1494	99%	200.0 µg/mL
Bis(2-chloroethoxy)methane	EB-1799	98%	200.0 µg/mL
Bis(2-chloroethyl)ether	EB-1500	99%	200.0 µg/mL
Bis(2-chloroisopropyl)ether	EB-1787	99%	200.0 µg/mL
Bis(2-ethylhexyl) phthalate	EB-0627	99%	200.0 µg/mL
4-Bromophenyl phenyl ether	EB-1003	99%	200.0 µg/mL
Butyl benzyl phthalate	EB-0702	98%	200.0 µg/mL
Carbazole	EB-0651	98%	200.0 µg/mL
p-Chloroaniline	EB-1264	99%	200.0 µg/mL
4-Chloro-3-methylphenol	EB-0222	99%	200.0 µg/mL
2-Chloronaphthalene	EB-1811	99%	200.0 µg/mL
2-Chlorophenol	EB-0216	99%	200.0 µg/mL
4-Chlorophenyl phenyl ether	EB-1771	99%	200.0 µg/mL
Chrysene	33385-57	99%	200.0 µg/mL
Dibenz(a,h)anthracene	35091-73	99%	200.0 µg/mL
Dibenzofuran	EB-0807	99%	200.0 µg/mL
Di-n-butyl Phthalate	EB-0687	99%	200.0 µg/mL
1,2-Dichlorobenzene	EB-1147	98%	200.0 µg/mL
1,3-Dichlorobenzene	EB-1745	99%	200.0 µg/mL
1,4-Dichlorobenzene	EB-1002	99%	200.0 µg/mL
3,3'-Dichlorobenzidine	EB-1812	99%	200.0 µg/mL
2,4-Dichlorophenol	EB-1772	99%	200.0 µg/mL
2,6-Dichlorophenol	EB-0339	99%	200.0 µg/mL
Diethyl Phthalate	EB-0686	99%	200.0 µg/mL
2,4-Dimethylphenol	EB-1773	99%	200.0 µg/mL
Dimethyl Phthalate	EB-1447	99%	200.0 µg/mL
2,4-Dinitrophenol[2]	EB-1486	98%	200.0 µg/mL
2,4-Dinitrotoluene	EB-1379	99%	200.0 µg/mL
2,6-Dinitrotoluene	EB-1311	99%	200.0 µg/mL
Dinoseb	ER042903-01	99%	200.0 µg/mL
Di-n-octyl Phthalate	27981-69	99%	200.0 µg/mL
Diphenyl ether	EB-1776	99%	200.0 µg/mL
1,4-Dioxane	EB-1335	99%	200.0 µg/mL
2-Ethoxyethanol	EB-1521	99%	200.0 µg/mL
Fluoranthene	32460-17	99%	200.0 µg/mL

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Component	Lot Number	Purity[1]	Concentration
Fluorene	35001-29	99%	200.0 µg/mL
Hexachlorobenzene	EB-0680	99%	200.0 µg/mL
Hexachloro-(1,3)-butadiene	EB-1777	99%	200.0 µg/mL
Hexachlorocyclopentadiene	EB-1159	96%	200.0 µg/mL
Hexachloroethane	EB-1299	99%	200.0 µg/mL
Hexachlorophene	EB-1485	95%	200.0 µg/mL
Hexachloropropene	EB-1792	99%	200.0 µg/mL
Indeno(1,2,3,-c,d)pyrene	35081-09	99%	200.0 µg/mL
Isophorone	EB-1778	98%	200.0 µg/mL
2-Methyl-4,6-dinitrophenol	EB-1404	99%	200.0 µg/mL
2-Methylnaphthalene	EB-0333	99%	200.0 µg/mL
2-Methylphenol	EB-1780	99%	200.0 µg/mL
4-Methylphenol	EB-1392	99%	200.0 µg/mL
Naphthalene	22599-76	99%	200.0 µg/mL
2-Nitroaniline	EB-0886	99%	200.0 µg/mL
3-Nitroaniline	EB-1782	99%	200.0 µg/mL
4-Nitroaniline	EB-0870	99%	200.0 µg/mL
Nitrobenzene	EB-2064	99%	200.0 µg/mL
2-Nitrophenol	EB-0227	99%	200.0 µg/mL
4-Nitrophenol	EB-1391	99%	200.0 µg/mL
N-Nitrosodi-n-butylamine	EB-0703	99%	200.0 µg/mL
N-Nitrosodiethylamine	EB-1798	99%	200.0 µg/mL
N-Nitrosodimethylamine	EB-1793	99%	200.0 µg/mL
N-Nitrosodi-n-propylamine	EB-1791	99%	200.0 µg/mL
N-Nitrosodiphenylamine	EB-1452	99%	200.0 µg/mL
N-Nitrosomethylethylamine	EB-1795	99%	200.0 µg/mL
N-Nitrosopiperidine	EB-1790	99%	200.0 µg/mL
N-Nitrosopyrrolidine	EB-0499	99%	200.0 µg/mL
Pentachlorobenzene	EB-1784	99%	200.0 µg/mL
Pentachloroethane	EB-1271/EB-1802	99%/95%	200.0 µg/mL
Pentachlorophenol	EB-0625	99%	200.0 µg/mL
Phenanthrene	35034-93	99%	200.0 µg/mL
Phenol	EB-1629	99%	200.0 µg/mL
Pyrene	22599-73	99%	200.0 µg/mL
Pyridine	EB-1289	99%	200.0 µg/mL
1,2,4,5-Tetrachlorobenzene	EB-1785	99%	200.0 µg/mL
2,3,4,6-Tetrachlorophenol	30319-21	99%	200.0 µg/mL
1,2,4-Trichlorobenzene	EB-1677	99%	200.0 µg/mL
2,4,5-Trichlorophenol	EB-0218	99%	200.0 µg/mL
2,4,6-Trichlorophenol	EB-1487	98%	200.0 µg/mL

[1] Chemical purity was determined by chromatographic analysis.
[2] These components can not be confirmed through chromatographic testing

Standard Solution Assay Parameters

Analysis Method:	GC/MS
Column:	DB-5ms, 30 m x 0.25 mm ID, 0.25 µm film thickness
Temp Program:	40°C (hold 4 mins) - 270°C @ 10°C/min (hold 11 mins)
Injector Temp:	Cool on-column
Detector Temp:	280°C

Each point analyzed in triplicate

Standard Solution Comparability and Homogeneity

Compound	*Concentration [3] (µg/mL) Early*	*Middle*	*Late*	*Mean*	*E, M, L % RSD*	*% Difference from Target*
Acenaphthene	206.7	201.2	196.2	201.4	2.6	0.7
Aniline	193.1	188.6	181.4	187.6	3.2	-6.2
Benzidine	Benzidine cannot be confirmed through chromatographic testing					
Benzo(a)pyrene	201.6	195.4	190.1	195.7	2.9	-2.1
Bis(2-ethylhexyl)phthalate	215.3	215.5	211.4	214.1	1.1	7.0
Carbazole	199.8	194.9	189.8	194.8	2.6	-2.6
4-Chloroaniline	204.9	197.8	191.9	198.2	3.3	-0.9
2-Chlorophenol	207.4	204.4	199.7	203.8	1.9	1.9
4-Chloro-3-methylphenol	204.1	200.3	194.0	199.5	2.6	-0.3
Dibenzofuran	201.4	196.3	191.4	196.3	2.6	-1.8
1,4-Dichlorobenzene	208.3	201.8	197.4	202.5	2.7	1.2
3,3'-Dichlorobenzidine	235.9	225.7	221.8	227.8	3.2	1.0 *
2,4-Dichlorophenol	211.6	209.4	203.0	208.0	2.1	4.0
2,4-Dinitrophenol	236.9	237.2	229.7	234.6	1.8	0.0 *
Diphenylamine	157.7	154.5	154.1	155.4	1.3	8.1 *
Fluoranthene	201.5	196.6	191.6	196.6	2.5	-1.7
Hexachloro-(1,3)-butadiene	205.4	197.8	193.7	198.9	3.0	-0.5
Hexachloroethane	206.8	201.7	197.8	202.1	2.2	1.1
Hexachlorocyclopentadiene	189.5	185.8	180.0	185.1	2.6	-7.4
Isophorone	208.0	201.8	197.4	202.4	2.6	1.2
2-Methyl-4,6-dinitrophenol	217.4	218.4	210.5	215.4	2.0	7.7
4-Nitroaniline	207.9	205.8	197.0	203.6	2.8	1.8
2-Nitrophenol	211.0	209.5	202.3	207.6	2.2	3.8
N-Nitrosodimethylamine	217.7	214.5	208.7	213.6	2.1	6.8
N-Nitrosodi-n-butylamine	209.3	206.0	200.1	205.1	2.3	2.6
Pentachlorophenol	195.4	194.7	191.0	193.7	1.2	-3.1
Phenol	204.4	197.0	193.8	198.4	2.7	-0.8
2,4,6-Trichlorophenol	206.1	204.5	198.1	202.9	2.1	1.4

* Component was analyzed in comparison to the existing standard

This standard was prepared from six stocks that have been verified for accuracy and homogeneity. Verification of this standard was performed by monitoring 28 components, including the Method 8270 Calibration Check Compounds (CCC) and at least two analytes from each stock standard.

Attachment 5.

Example: 3,3'-Dimethylbenzidine

Cerilliant
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ERD-132S
ER031605-02
Revision 0

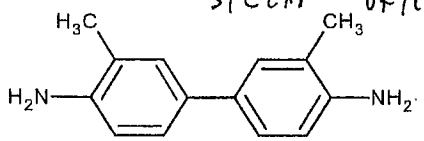
Certificate of Analysis

EXDMB SPP...12

06GPLDMBA

Acc: 07/24/06
STD EXP: 07/24/07

3,3'-Dimethylbenzidine



Catalog Number:	ERD-132S
Solution Lot:	ER031605-02
Expiration Date:	March 2008
Solvent:	Methylene chloride
Amount per Ampule:	1.2 mL
Storage:	Protect from light, store in freezer.
Handling:	We advise laboratories to use measured volumes of this standard solution before diluting to the desired concentration.
Intended Use:	For laboratory use only. This product is a quantitative standard useful for calibration, quality control, and other general applications requiring accurate solutions.

Component	Purity[1]	Prepared Concentration[2]	Analyzed Concentration[3]
3,3'-Dimethylbenzidine	99%	2000 ± 62 µg/mL	1973 ± 30 µg/mL

Standard Solution Comparability

Standard Solution	*Lot Number*	*% Difference from New Lot*
New Lot	ER031605-02	
Previous Lot	ER060404-01	-1.9

Standard Solution Homogeneity

Ampuling Position	*Concentration[3] (µg/mL)*	*Mean*	*% RSD*
Early	1973		
Middle	1977		
Late	1969	1973	0.2

1 Chemical purity was determined by chromatographic analysis. See following pages for more information.

2 The range of the prepared concentration is determined by statistical process control of our production and analysis systems with a 95% confidence.

3 Concentration values are determined by comparison to an independent calibration curve. We suggest using the prepared concentration value for dilutions. The concentration range is calculated from the distribution of multiple analyses of the new standard with a 95% degree of confidence.

Cerilliant certifies that this standard meets or exceeds the specifications stated in this data sheet. Accuracy is ensured by exhaustive purity determinations and gravimetric preparation using balances calibrated with NIST traceable weights. Precision is guaranteed by triplicate analysis and comparison to previous lots (when available). Finally, homogeneity is demonstrated by random analysis of the ampuled standard.

Authorized Signature: Lara Sparks

Lara Sparks, Quality Assurance Director

April 8, 2005

Date

Appendix 1

JP4 and JP8

The JP4 or JP8 extraction is nearly identical to the DRO Soxtherm procedure. Follow the DRO extraction procedure making the appropriate changes as noted in this appendix.

1.0 Surrogate and Matrix Spike Solutions

1.1 DRO Surrogate Spike Solution

The surrogate used for the JP4 or JP8 extraction is the same solution used for the DRO extraction. The surrogate used in the extraction of DRO from waters is a solution of 2-Fluorobiphenyl and o-Terphenyl in acetone at the concentrations listed below. The GC group prepares the working surrogate solution. 500 uLs of DRO Surrogate Spike Solution is added to all samples, MBs, LCS and MS/MSD.

Compound	Concentration (ug/mL)
2-Fluorobiphenyl	100
o-Terphenyl	100

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

1.2 JP4 Matrix Spike Solution

The LCS/MS solution used in the extraction of JP4 from waters is a solution in methanol. The composition and concentration of this standard is beyond the scope of this SOP. See the analytical SOP for specifics about this standard. 500 uLs of JP4 Spike Solution is added to LCS and MS/MSD.

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

1.2 JP8 Matrix Spike Solution

The LCS/MS solution used in the extraction of JP8 from waters is a solution in methanol. The composition and concentration of this standard is beyond the scope of this SOP. See the analytical SOP for specifics about this standard. 500 uLs of JP8 Spike Solution is added to LCS and MS/MSD.

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

2.0 Soxtherm Extraction

2.1 Extraction solvent system change in section **7.6.2.2.5**. Use DCM as the extraction solvent. Acetone will interfere with the earlier peaks on the jet fuel chromatogram.

2.2 As in section **7.6.2.3.9**, add the metal cooling grid when the extract reaches the desired volume. However, since DCM is the extraction solvent, the extract will continue to concentrate with the grid in place more so then with the DCM:acetone solvent system. The extracts must be continuously watched during the cooling phase to ensure that the extract volume does not go below 10 mLs.

Appendix 2

AR1242 and AR1254 PCBs

Other than having different matrix spike standards, the AR1242 and AR1254 extraction is identical to the PCB Soxtherm extraction.

1.0 Matrix Spike Solutions

These two matrix spike solutions need to be used separately. Samples batches will contain an LCS/MS/MSD for AR1242 and an LCS/MS/MSD for AR1254.

1.1 AR1242 Spike Solution

The LCS/MS solution used in the extraction of PCBs from soil/sediments is a solution of Arochlor 1242 in methanol at the following concentrations. 500 uLs of PCB Spike Solution is added to the LCS and MS/MSD.

Compound	Concentration (ug/mL)
AR 1242	5.0

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

1.1 AR1254 Spike Solution

The LCS/MS solution used in the extraction of PCBs from soil/sediments is a solution of Arochlor 1254 in methanol at the following concentrations. 500 uLs of PCB Spike Solution is added to the LCS and MS/MSD.

Compound	Concentration (ug/mL)
AR 1242	5.0

- Life of Standard: Same as parent solution.
- Storage Requirements: As stated in Section 5.2.

SOP No.	Revision No.	Date	Page
USP-5035	05	10/06/06	1 of 12

TITLE: Laboratory Handling, Transfer and Preservation of VOA Soil Samples Received in EnCore™ Samplers for SW-846 Method 5035 Low Concentration and 5030B

Updated by:	Signature:	Date:
JoAnn M. Petruszak-Kmetty GC/MS Supervisor; GC VOA		10-5-06

Approved by:	Signature:	Date:
Jodi Gromala Organic Dept. Manager		10-5-06
David W. Mazur Env. Health & Safety Coor.		10/5/06
Terese A. Preston Quality Manager	Terese A. Preston	10/5/06

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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) has been written using SW-846 Methods 5035 and describes the procedures for handling, transferring and preserving solid waste, soil and sediment samples for subsequent determination of volatile organic compounds when received by the laboratory in EnCore™ Disposable Samplers. The EnCore™ Sampler is a single use device which cannot be cleaned and/or reused. Samples are transferred to vials and are then suitable for analysis using preparation Methods 5035 for Low Concentration volatile compounds or 5030B for High Concentration volatile compounds. This procedure also addresses issues relating to VOC samples preserved in the field using Method 5035, however, does not discuss sample collection.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be discussed with the project manager and a job note would be added to the Labnet/LIMs (LIMS) project. This note would then carry over to any job that is logged in against the project, and mentioned in the data package's case narrative.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

Refer to the analytical SOPs.

1.1.2 Reporting Limits

Refer to the Analytical SOPs.

1.2 Summary of Method

This procedure is used when soils are sampled in the field with EnCore™ samplers and then transferred to the laboratory for preservation. The specific preparation procedures for sample vials depends on the expected concentration range of the sample, with separate procedures for "low" concentration soil samples (Section 7.1) and "high" concentration soil samples (Section 7.2). Low concentration soils are transferred to vials containing sodium bisulfate and water which forms an acid for preserving the VOC from biodegradation prior to sample preparation method 5035. High concentration VOC soils are transferred to vials containing methanol prior to sample preparation 5030B.

1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

2.0 INTERFERENCES

Solvents, reagents, glassware and room conditions may yield volatile organic compounds. All these materials must be demonstrated to be free from interferences under the conditions of the preparation by analyzing method blanks.

3.0 SAFETY

- Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

- Take careful note of those sections marked "CAUTION", "NOTE", OR "WARNING".
- When the sample is added to the vial containing sodium bisulfate and organic free water, a reaction can result with pressure build-up if the sample is immediately capped. This may result in the popping of the septum cap and splashing of corrosive liquid (acid) and, under severe pressure, may burst the sample vial. If effervescence is noted, the sample vial shall not be sealed until the reaction is complete or ends. All samples demonstrating effervescence shall be prepared in organic free water with a note in Labnet/Lims that the sample effervesced.

3.2 Primary Material Used

- The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	OSHA Exposure Limit	Signs and symptoms of exposure/Unusual Hazards
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.

4.0 EQUIPMENT AND SUPPLIES

- 40-ml, screw-cap, PTFE lined, septum-sealed glass vials
- Magnetic stir bars
- EnCore™ Extrusion Tool
- Top-loading balance capable of accurately reading to 0.01 g.
- Balance weights
- 5 g En Core™ samplers (from field in sealed containers)
- Pliers for removing En Core™ Sampler locking arms.
- Repipet suitable for dispensing methanol
- Repipet suitable for dispensing lab pure water
- 1 gram scoop; and VOC vial rack

5.0 REAGENTS AND STANDARDS

A label on any reagent bottle must contain the concentration of the reagent, name of the reagent, date prepared, expiration date and the analyst who prepared the reagent.

5.1 Reagents

- Methanol, CH_3OH - purge and trap quality of equivalent
- Organic Free Laboratory Water (OFW)
- Sodium Bisulfate, $NaHSO_4$ - ACS grade or equivalent

5.2 Quality Control (QC) Solutions

Refer to analytical SOPs.

6.0 CALIBRATION

Not Applicable.

7.0 PROCEDURE

7.1 Low Concentration Procedure

The following steps apply to the preparation vials and EnCore™ sample transfers to vials that will be analyzed for low concentration volatile compounds by the closed-system purge and trap equipment described in Method 5035.

7.1.1 Low Concentration Sample Vial Preparation

Ready-to-use sample vials for the low-level method may be purchased from a vendor which contains the sodium bisulfate preservative, water, magnetic stirrer and tare weighted. If not, steps described in 7.1.1 are to be followed to prepare the vials.

7.1.1.1 Add a clean magnetic stir bar to each clean 40 mL vial. Add 5 mLs of a 20% sodium bisulfate solution (200g sodium bisulfate/Liter OFW). Enough sodium bisulfate should be present to ensure a sample pH of ≤ 2.

7.1.1.2 The water and preservative form an acid solution that will eliminate the majority of the biological activity in the sample, preventing biodegradation of the volatile target analytes. Seal the vial with the screw-cap septum seal.

7.1.1.3 Since calcareous soils may react vigorously with sodium bisulfate, which could result in a loss of volatile compounds, an effervescence test will be performed prior to sample preparation. Add ~5 grams of sample to an empty 40-mL vial. Add ~5 mLs of 20% sodium bisulfate solution to the vial. Observe for bubbles. If the sample effervesces, then prepare the sample in OFW and freeze instead of preparing in sodium bisulfate. A note should be made in Labnet/LIMs and in the Sample Weight Prep Log that the sample effervesced and was prepared in organic free water.

WARNING: When the sample is added to the vial containing sodium bisulfate and organic free water, a reaction can result with pressure build-up if the sample is immediately capped. This may result in the popping of the septum cap and splashing of corrosive liquid (acid) and, under severe pressure, may burst the sample vial. If effervescence is noted, the sample vial shall not be sealed until the reaction is complete or ends. Acid solution can cause burns, therefore, protective gloves, lab coat and eye protection shall be worn during this transfer.

7.1.1.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight and vial number in Labnet/LIMs. Record the job number, client, date, Labnet/LIMs prep batch, analyst initials and comments in the Sample Weight Prep Log. The vial is then ready for transferring the soil sample from the EnCore™ sampler into the vial as described in section 7.1.2.

7.1.2 Sample Transfer from EnCore™ to Low Concentration Vial

7.1.2.1 Within 48 hours of sample collection, the sample in the EnCore™ sampler must be transferred to the sample vial containing preservative or OFW depending on the effervescence test. Line up the EnCore™ sample bags with vials and record the respective sample # on the vial and in Labnet/LIMs. Perform the effervescence test and record the results in Labnet/LIMs and the comment sections in the prep logbook.

7.1.2.2 Remove the EnCore™ sampler from its sealed bag and break off the locking arms on the cap using pliers. Do not remove the cap at this time.
(**CAUTION: Broken edges will be sharp**).

7.1.2.3 Attach the EnCore™ Sampler to the EnCore™ Extrusion Tool as follows: Depress the locking lever on the Extrusion Tool and place the sampler, plunger end first, into the open end of Extrusion Tool (aligning slots on sampler body with pins in Extrusion Tool). Turn the coring body clockwise until it locks into place. Then release the locking lever.

7.1.2.4 Place the soil core plug into the matching vial: Remove the cap from the vial and then remove the cap from the EnCore™ Sampler, which was previously inserted in the Extrusion Tool. Slowly place the sample core directly over the vial (avoid sample or vial spillage), then release the soil core by pushing down on the plunger knob of the EnCore™ Extrusion Tool. Cap the vial if sample effervescence is not apparent. In Labnet/LIMs, record the time the sample was transferred into the vial. After the sample is safely transferred, remove and properly dispose of the EnCore™ Sampler.

If samples are received already preserved from the field and they show evidence of effervescence (i.e., bulging septa, fizzing, hissing when auto-sampler punctures septa, etc.), the analyst shall notify the PM at once. Additionally, the analyst needs to proceed with the analysis using either Method 5030B purge & trap using an appropriate aliquot from the VOA jar or solids jar if available or in cases where the client provides both sodium bisulfate preserved sample and OFW prepared samples use the OFW and document the reason in the prep logbook.

7.1.2.5 Weigh the sample vial to the nearest 0.01 g and record weight in Labnet/Lims. The sample is then transferred to the GC/MS VOC refrigerator if preserved in sodium bisulfate or transferred to the GC/MS VOC freezer if prepared in water.

NOTE: Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes and internal standards should be added through the septa after the vial has been capped. These standards will be introduced by the GC/MS VOC analyst or automatically by the sample introduction system, just prior to analysis.

7.2 High Concentration Procedure

The following steps apply to the preparation vials and En Core™ sample transfer to these vials to be analyzed for High concentration volatile compounds described in Method 5030B.

7.2.1 High Concentration Sample Vial Preparation

Sample vials ready for use for the high concentration method may be purchased from a vendor which contains the methanol preservative and tare weighted. If not, steps described in 7.2.1 are to be followed to prepare the vials.

7.2.1.1 Add 5 mLs of methanol to each vial. **NOTE: Any combination of sample weight and methanol volume may be used as long as it is demonstrates that method performance objectives can be achieved.**

7.2.1.2 Seal the vial with the screw-cap septum seal and affix a label to the vials.

7.2.1.3 Weigh the prepared vial to the nearest 0.01 g, record the tare weight and the vial number in Labnet/LIMs. The vial is then ready for transferring the soil sample from the EnCore™ sampler into the vial as described in Section 7.2.2.

7.2.2 Sample Transfer from En Core™ Sampler to High Concentration Vial

7.2.2.1 Within 48 hours of sample collection, the sample in the EnCore™ sampler must be transferred to the sample vial containing preservative. Line up the EnCore™ sample bags with vials and record in Labnet/LIMs the respective sample #.

7.2.2.2 Remove the EnCore™ sampler from its sealed bag and break off the locking arms on the cap using pliers, but do not remove cap at this time.
(CAUTION: Broken edges will be sharp).

7.2.2.3 Attach the EnCore™ Sampler to the EnCore™ Extrusion Tool as follows: Depress the locking lever on the Extrusion Tool and place the sampler, plunger end first, into the open end of Extrusion Tool (aligning slots on sampler body with pins in Extrusion Tool). Turn the coring body clockwise until it locks into place. Then release the locking lever.

7.2.2.4 Place the soil core plug into the matching vial: Remove the cap from the vial and then remove the cap from the EnCore™ Sampler, which was previously inserted in the Extrusion Tool. Slowly place the sample core directly over the vial (avoid sample or vial spillage), then release the soil core by pushing down on the plunger knob of the En Core™ Extrusion Tool. Cap the vial but be careful not to spill. **(WARNING: Precautions must be taken when handling vials and samples. Methanol is flammable and should not be handled near a heat source or open flame. Protective gloves, lab coat and eye protection shall be worn during this transfer.)** In Labnet/LIMs, record the time the sample was transferred into the vial. After the sample is safely transferred, remove and properly dispose of the EnCore™ Sampler.

7.2.2.5 Weigh the sample vial to the nearest 0.01-g and record the weight in Labnet/LIMs. The sample is then transferred to the GC/MS VOC refrigerator for 24 hours. After the 24 hour contact time, draw off the methanol and put into a 1.5 mL amber vial labeled with the appropriate sample identification. Record the time the methanol is drawn off in the logbook. Surrogates, matrix spikes and internal standards should be added by the auto-sampler or the GC/MS VOC analyst at the time of analysis.

7.2.2.6 In cases where the client requires a quick turnaround time, the 24-hour contact time can be replaced by sonicating the samples for 20 minutes and then draw of the methanol. This procedure requires the client's approval.

7.3 Quality Control Checks

Refer to the analytical SOP.

7.4 Sample Preservation and Storage

The hold time for the extraction of volatile organic compounds from soils and sediments is 14 days from the date of sampling. The samples must be transferred from the EnCore™ Sampler to the preservatives or OFW and vial within 48 hours after collection. Preserved samples must be stored at 4 $\pm$ 2°C prior to analysis. Samples in OFW must be frozen at -10 $\pm$ 2°C. Frozen samples must be allowed to come to room temperature before analysis.

7.5 Calibration / Standardization

Not Applicable.

7.6 Preventive Maintenance

- Balances should be cleaned and checked for levelness prior to each use. Class "S" weights must be weighed and documented each day the balance is used. Refer to the Balance Calibration Logbook for the weights and control limits.
- Consult your section manager or supervisor if the weights are out of acceptable limits. Do not use the balance until the situation is back in control.

7.7 Documentation

All sample transfer information must be carefully documented in Labnet/LIMs. Record the job number, client, date, 5035PL batch, 5035PH batch, analyst initials and comments in the sample weight prep log. All problems and/or deviations from normal procedures must be documented, the section manager or supervisor should be notified and if the situation warrants it, a Sample Discrepancy Report (SDR)/Nonconformance Memo (NCM) may need to be initiated.

8.0 QUALITY CONTROL

8.1 QC Summary

Refer to the analytical SOP (UMV-8260).

8.2 Corrective Actions

All problems and/or deviations from the normal procedure must be documented in the Sample Weight Prep Log and in the comment section in Labnet/LIMs. The section manager or supervisor should be notified and an SDR/NCM may need to be initiated.

9.0 DATA ANALYSIS AND CALCULATIONS

Not Applicable.

10.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

- All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

10.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Residual samples waste containing Methanol. This residual sample waste containing methanol will be turned into the Waste technician for disposal in the "Flammable Vials" wastestream.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.

13.0 ATTACHMENTS

Attachment A: Example: EnCore™ GC/MS and GC VOA Sample Weight Prep Log
Attachment B: Example: Batch Data

Historical File:

Revision 00: 02/27/98
Revision 01: 06/16/99
Revision 02: 06/22/01
Revision 03: 04/11/03
Revision 04: 03/08/05
Revision 05: 10/05/06

Reasons for Change, Revision 05:

- Annual Review – Changed reference from Labnet to LabNet/LIMs
- Section 8.2 - Added reference to NCMs

U:\QC\SOP\SP\5035.DOC

Attachment A.

Example: VOC Sample Log
(011-001)

STL Chicago

GC/MS and GC Volatile: Sample Weight Prep Log

Page: _____

Job #	Client	Date	5035PL Batch	5030PH Batch	Comments (# of vials)	Analyst

Reviewer Signature: _____ Date: _____

CHI-22-20-056\A-09/04

Attachment B.

Example: Batch Data
(012-001 to 012-004)

5035 Preservation Low
Method Code..: 5035PL
Batch Code...: 190708

Status.....: RVWD
Batch Date...: 10/06/06
Batch Time...: 334

User Name.....: wre
QC Code.....:
Calc Code.....: PREPPL

Location Code..: 57222
Equipment Code.:
Import Code....:

SAMPLE: Grp Pos	Sample ID	Dilution	TEST CODE / TEST POS Date / Time	PRES 1	PRESW 2
1 1	249015_1_S___		10/6/06 0340	0	0
1 2	249015_1_S___		10/6/06 0340	0	0
1 3	__S_EB3__		10/6/06 0340	0	0

5035 Preservation Low Report Date: 10/8/06 11:18

Method Code..: 5035PL	Batch Date...: 10/06/06	QC Code.....:	Equipment Code.:
Batch Code...: 190708	Batch Time...: 334	Calc Code.....: PREPPL	Import Code....:
Status.....: RVWD	User Name....: wre	Location Code..: 57222	

BATCH:	Item	Description	Description Information
	1	MeOH	na
	2	NaHSO4	na
	3	Balance #	p-214
	4	Repipetor Vol. Check	
	5	Methanol	na
	6	H2SO4	na
	7	Water	ok

SAMPLE:	Grp	Pos	Sample ID	Dilution	PRES Text	PRESW Text	WEIGHT g	IWGT g	FWGT g
	1	1	249015_1_S___		x	a	4.766	30.7282	35.4938
	1	2	249015_1_S___		x	b	5.646	30.6227	36.2690
	1	3	__S_EB3__		x	x	5.000	30.00	35.00

SAMPLE:	Grp	Pos	Sample ID	Dilution	PREPF N/A	DLFAC N/A	EFFERV yes/no	FIELDP Text	
	1	1	249015_1_S___		1.0491	1.0491	yes		
	1	2	249015_1_S___		0.8856	0.8856	yes		
	1	3	__S_EB3__		1.0000	1.0000	na		

012-002

*** RUN LOG *** (V2)

10/8/06 11:1?

5035 Preservation High (Methanol)
Method Code..: 5035PH
Batch Code...: 190709

Status.....: RVWD
Batch Date...: 10/06/06
Batch Time...: 342

User Name.....: wre
QC Code.....:
Calc Code.....: PREPFV

Location Code..: 57222
Equipment Code.:
Import Code....:

			TEST CODE	PRES																			
SAMPLE: Grp Pos	Sample ID	Dilution	TEST POS Date / Time	1																			
1 1	249015_1_H___		10/6/06 0340	0																			
1 2	__H_EB2__		10/6/06 0340	0																			

012-003

5035 Preservation High (Methanol) Report Date: 10/8/06 11:18

Method Code..: 5035PH	Batch Date...: 10/06/06	QC Code.....:	Equipment Code.:
Batch Code...: 190709	Batch Time...: 342	Calc Code.....: PREPFV	Import Code....:
Status.....: RVWD	User Name....: wre	Location Code..: 57222	

BATCH:	Item	Description	Description Information
	1	MeOH	cp805
	2	NaHSO4	na
	3	Balance #	p-214
	4	Repipetor Vol. Check	
	5	Methanol	ok
	6	H2SO4	na
	7	Water	na

SAMPLE:	Grp	Pos	Sample ID	Dilution	PRES Text	WEIGHT g	IWGT g	FWGT g	MEVOL mL
	1	1	249015_1_H___		c	5.622	28.8117	34.4335	5
	1	2	__H_EB2__		x	5.000	30.00	35.00	5

SAMPLE:	Grp	Pos	Sample ID	Dilution	EXTVOL mL	H2OVOL mL	PREPF N/A	DLFAC N/A	FIELDP Text
	1	1	249015_1_H___		0.1	5	44.4682	0.8894	
	1	2	__H_EB2__		0.1	5	50.0000	1.0000	

012-004

METALS DIGESTION/PREPARATION

METHODS

USEPA SW846

3005A, 3010A, 3030C, 3031, 3050B

USEPA CLPILM 04.1 Aqueous & Soil/Sediment (NJDEP does not accept CLPILM 04.1 after June, 2003)

Addendum for USEPA CLPILM 05.2 Aqueous & Soil/Sediment

USEPA Methods for Chemical Analysis of Water and Wastes

200.7, Standard Methods 3030C

SOP NUMBER: SOP-100

REVISION NUMBER: 19

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

07/25/06
EFFECTIVE DATE

07/25/06
DATE OF LAST REVIEW

METALS DIGESTION/PREPARATION

References:
Methods 3005A/USEPA CLPILM0 4.1 Aqueous, 3010A, 3030C, 3031, 3050B
USEPA CLPILM0 4.1 (Soil/Sediment), 200.7, Standard Methods 3030C
See Addendum for USEPA CLPILM 05.2 (Aqueous & Soil/Sediment)

I. SCOPE AND APPLICATION

A. AQUEOUS

1. Method 3005A and USEPA CLP ILM0 4.1, "Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by ICP Spectroscopy".

   a. This method is used to prepare surface water, ground water, drinking water and wastewater samples for analysis by inductively coupled argon plasma spectroscopy (ICP).

2. Method 200.7, "Determination of Metals and Trace Metals in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry"

   a. This method is used to prepare surface water, ground water, drinking water and wastewater samples for analysis by inductively coupled argon plasma spectroscopy (ICP).

3. Method 3010A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy".

   a. This method is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis by ICP. The procedure is used to determine total metals.

4. Method 3030C (Standard methods), "Preliminary Treatment for Acid-Extractable Metals".

   a. This method is used to prepare ground water samples from North Carolina for analysis by ICP.

B. SOLIDS

1. Method 3050B, "Acid Digestion of Sediments, Sludges and Soils".

   a. This method is used to prepare sediments, sludges and soil samples for analysis by ICP. Since certain matrices may result in poor recovery, the method of standard additions may be used when analyzed.

   b. It should be noted that some metals could be biased high with the soil digestion when dilution is necessary. Take necessary measures to ensure that dilutions are made as accurately as possible.

2. USEPA CLP ILM0 4.1, "Acid Digestion of Soil/Sediment"

   a. This method is used to prepare sediments and soil samples for analysis by ICP. Since certain matrices may result in poor recovery, the method of standard additions may be used when analyzed.

C. OILS

1. Method 3031, "Digestion Procedure for Oils".

   a. This method is used to prepare samples containing oils, greases or waxes for analysis by inductively coupled argon plasma emission spectroscopy (ICP).

D. **NOTES:**

1. "Total Metals" includes all metals, inorganically and organically bound and both dissolved and particulate.

2. "Dissolved metals" includes all metals present in a sample after filtration through a 0.45 micron filter followed by digestion.

II. SUMMARY OF METHODS

A. A representative sample of water, soil or oil is put into an acid medium and exposed to heat for a certain amount of time. This allows for reduction of interferences by organic matter and converts metals bound to particulates to form the free metal that can be determined by ICP-Atomic Emission Spectrometry.

NOTE: When a reporting limit is required for a project lower then is customary, a four times concentration must be used in order to reach that lower level. Care

must be taken to matrix match this concentrated aliquot. A blank and laboratory control sample (at a reduced concentration) are required with this concentration as well as a matrix spike (at a reduced concentration) and duplicate or matrix spike, matrix spike duplicate per 20 samples.

III. SAMPLE HANDLING AND PRESERVATION

A. AQUEOUS

1. Samples are taken in high density polyethylene, one liter bottles. Samples should be preserved with concentrated HNO_3 to a pH <2 immediately once sampled. If dissolved metals are to be analyzed the sample should be filtered before the HNO_3 is added. The samples should be maintained at 4°C until analysis. The holding time for metals samples is 180 days or approximately 6 months.

B. SOLIDS

1. Samples are taken in high density polyethylene(CLP only) or glass bottles. The samples should be maintained at 4°C until analysis. The holding time for metals samples is 180 days or approximately 6 months.

C. OILS

1. Samples are taken in high density polyethylene bottles. The samples should be maintained at 4°C until analysis. The holding time for metals samples is 180 days or approximately 6 months.

IV. INTERFERENCES

A. AQUEOUS

1. Method 3005A and USEPA CLPILM0 4.1, "Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by ICP Spectroscopy", SW846, July, 1992.

   a. This digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

2. Method 200.7

3. Method 3010A

   a. See method 6010B.

B. SOLIDS

1. Method 3050B

   a. Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether this method is applicable to a given waste.

2. USEPA CLP ILM0 4.1

   a. Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether this method is applicable to a given waste.

C. OILS

1. Method 3031

   a. These digestates can have very high dissolved solids, which may necessitate the use of internal standards, dilutions, or the method of standard addition.

V. SAFETY

A. Normal accepted laboratory safety practices should be followed while performing this analysis.

B. Be certain the exhaust hood is functioning before you begin the digestion procedure.

C. Hot acids can be extremely corrosive. Avoid inhalation or contact with skin.

VI. EQUIPMENT/APPARATUS

A. Fume hood, Labconco or equivalent.

B. Hot plate, Thermolyne cimarec-3 or equivalent source for use at 95°C. The temperature of the hot plate must be monitored via the use of a temperature blank.

C. Thermometer capable of reading 80 to 120 degrees C – ERTCO cat# 611-3-SC or equivalent.

D. Vacuum pump for filtering dissolved metals- Gast or equivalent.

E. Analytical balance capable of weighing to 0.01 gram. Mettler model BB300 or equivalent.

F. Beckman CS-6R centrifuge.

G. Various class A volumetric glassware and ribbed watchglasses, Pyrex or equivalent.

H. Whatman No. 41 filter paper or equivalent.

I. Whatman No. 42 filter paper or equivalent.

J. Whatman 0.45 micron filter paper or equivalent.

K. 250 mL beaker or other appropriate vessel such as polypropylene block digester tubes, watch glasses and caps.

L. Stirring device, e.g. magnetic stirrer, glass rod or equivalent.

M. Manual Sample Mill

N. Wiley Sample Mill

O. Clippers for cutting vegetation

NOTE: All glassware should be acid washed.

VII. REAGENTS AND STANDARD PREPARATION

A. REAGENTS

1. Metals grade Nitric acid (HNO_3). Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

2. Metals grade Hydrochloric acid (HCl). Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

3. 30% hydrogen peroxide reagent, ACS Grade. Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

4. Metals grade Sulfuric acid (H_2SO_4). Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

5. Reagent water (Deionized water).

6. Potassium Permanganate - Ultra pure grade. Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

7. Ammonium hydroxide, concentrated, reagent grade. Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

8. Ammonium phosphate, reagent grade- Reagent should be analyzed to determine level of impurities. If method blank is <MDL, then the reagent can be used.

9. Base oil, analyte-free. Oil should be analyzed to determine level of impurities. If method blank is < MDL, then the reagent can be used.

B. STANDARDS

1. Traceability

a. A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

b. All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date and the logbook where information is recorded. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

c. The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

2. PREPARATION

A. Laboratory control sample

1. Aqueous

a. This solution is prepared as follows: 50 mL concentrated HCl, 20 mL concentrated HNO_3, 1 mL of CLP-CAL-1, Solution A, 1 mL of CLP-CAL-1 Solution B, 0.25 mL of CLP-CAL-2, and 0.25 mL of CLP-CAL-3 diluted to 1 L in a volumetric flask. Use 50 mL (100 mL for strict CLPIIM0 4.1) for digestion. This solution is given a unique identifier and recorded in sample digestion logbook.

b. For four times concentrated samples: The solution is prepared as follows: 50 mL concentrated HCl, 20 mL concentrated HNO_3, 1mL CLPP-SPK-4 (Inorganic Ventures) (This solution contains 10 mg/L Selenium, 100 mg/L Antimony, 50 mg/L Cadmium and Thallium, 40 mg/L Arsenic and 20 mg/L Lead) to 1 L in a volumetric flask. This solution is given a unique identifier. Use 12.5 mLs to 50 mLs and prepare two aliquots. Heat at 90 to 95°C to reduce the volume in each vessel to ten mLs and then combine each 10 mL aliquot into one vessel and take to a final volume of 25 mLs. Take care to matrix match acids so that the final 25 mL portion will contain 2% HNO_3 and 5% HCl. Use 0.125 mLs HNO_3 and 0.3125 mLs HCl to each 50 mL vessel.

2. Solids

a. A 1.0 ±0.02 gram aliquot of teflon chips is weighed and spiked using the same spiking solution used for matrix spikes. This sample is given a unique identifier according to the Lot# for the teflon chips used and when digested is given the descriptor. i.e. LCSS(date)A and then B etc. plus the unique identifier number assigned. Alternatively a solid matrix standard reference material is obtained from the manufacturer. This sample is given a unique identifier and recorded in the sample digestion logbook.

3. Oils

a. **An analyte free oil MUST be used or explosive reactions can occur.** An analyte free oil (wesson oil which has been analyzed previously to prove that it is < MDL.) is spiked using the same spiking solution used for matrix spikes. This sample is given a unique identifier. i.e. LCSO(date)A and then B etc.

B. Spiking solution

1. Sample is spiked using 0.1 mL of CLP-CAL-1, Solution A, 0.1 mL of CLP-CAL-1 Solution B, 0.025 mL of CLP-CAL-2 and 0.025 mL of CLP-CAL-3 for a final volume of 100 mL. If only 50 mL is used, decrease amount used appropriately. These solutions are given unique identifiers. Record the amount spiked and the unique identifier of the standard.

2. CLP sample is spiked using 0.1 mL CLPP-SPK-1 and 0.1 mL CLPP-SPK-4 for a final volume of 100 mL. If only 50 mL is used, decrease amount used appropriately. These solutions are given unique identifiers.

3. For samples that require four times concentration, the sample is spiked using 0.0125 mLs of CLPP-SPK-4 to each of two vessels with 50 mLs of sample in each. The volume of each of the vessels is lowered to less then 10 mLs and combined and the final volume of this concentrated sample is 25mLs.

VIII. CALIBRATION

A. The temperature of the samples must be maintained at 95°C and monitored via a temperature blank. 85° for oil samples. Record in digestion logbook.

IX. PROCEDURE

A. Glassware preparation for oil digestion or when the hot-block can not be used:

1. Wash glassware with hot soapy water and rinse thoroughly. (Beakers must be washed as soon as possible after being used, dirty beakers must not be allowed to sit overnight.)

2. Rinse glassware with reagent water that contains 5% HNO_3 and 5% HCl followed by a rinse with reagent water.

3. Prior to use, all glassware must be confirmed clean via a glassware check. Otherwise, repeat step "2" until the glassware check passes.

B. Aqueous sample filtration (for dissolved metals):

1. Thoroughly clean a flask and funnel with hot soapy water. Next, rinse the flask and funnel with 1:5 HNO_3 followed by a thorough D.I. water rinsing. This step is very important because the filters contain some metals (namely Zn) which could contaminate the samples.

2. Rinse a 0.45 micron filter with 1:5 HNO_3 thoroughly, followed by D.I. water.

3. Filter the unpreserved sample. If dissolved Hg analysis is requested for the sample, filter at least 200 mL.

4. Discard the first 50 to 100 mL.

5. A preparation blank must be taken through the filtration step and analyzed with the sample.

6. Preserve the sample with HNO_3 to pH<2.

7. Soluble samples that are clean and clear do not have to be digested. Use 100 mL sample, add 5 mL of concentrated HCl and 2 mL of concentrated HNO_3. **Samples must be digested unless approval for analysis without digestion is received from the project manager.**

C. Aqueous sample preparation

1. Method 3005A and USEPA CLP ILM0 4.1, "**Acid digestion procedure for total recoverable or dissolved metals for analysis by ICP ".**

a. Shake sample thoroughly and pour 50 mL of the well-mixed sample into a digestion vessel. For samples which require concentration pour 50 mLs of the well-mixed sample into two digestion vessels.

b. Add 0.50 mL (1 mL of (1+1) when strict CLP ILM0 4.1 is required) concentrated HNO_3 to the sample. For samples which require concentration, add 0.125 mL (0.25 mL of (1+1) when strict CLP ILM0 4.1 is required) concentrated HNO_3 to the sample.

c. Add 2.5 mL (5 mL of 1+1) when strict CLP ILM0 4.1 is required) concentrated HCl to the sample. For samples which require concentration, add 0.3125 mL (0.625 mL of (1+1) when strict CLP ILM0 4.1 is required) concentrated HCl to the sample.

d. Cover the sample with a ribbed watch glass or equivalent source.

e. Transfer the digestion vessel to a pre-heated hot plate or hot block at 90 to 95°C. A temperature blank will assure correct temperature. The temperature must be recorded in the digestion log book. Take the volume down to between 5 to 10 mL, (12 to 25 mLs when strict CLP ILM0 4.1 is required) **making certain that the sample does not boil. This is extremely important. Boiling may lead to vaporization of certain analytes.** Remove the sample from the hot plate and cool

f. When necessary, filter or centrifuge the sample to remove insoluble material that could clog the nebulizer. The filtering apparatus must be thoroughly cleaned with dilute nitric acid prior to filtration.

g. Bring sample to its predigestion volume (or when samples require concentration, to a volume four times lower then what was started with) with DI water in the digestion vessel. The final volume must be recorded in the digestion log book.

h. The sample is now ready for analysis.

i. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards plus identification #'s for standards used for spiking and the volume spiked into the sample.

2 Method 200.7, "**Acid digestion procedure for total recoverable metals**".

a. Shake sample thoroughly and pour 50 mL of the well-mixed sample into the digestion vessel. If sample contains undissolved solids >1% refer to Section 11.3 of Method 200.7 for subsequent procedures.

b. Add 1.0 mL concentrated HNO_3 to the sample.

c. Add 2.50 mL concentrated HCl to the sample.

d. Cover the sample with a ribbed watch glass or equivalent source.

e. Transfer the digestion vessel to a pre-heated hot plate or equivalent source at 85°C. Take the volume down to between 10 to 15 mL, **making certain that the sample does not boil. This is extremely important. Boiling may lead to vaporization of certain analytes.**

f. Leave sample on hot plate and gently reflux for 30 minutes. Remove from hot plate and cool.

g. Bring sample to its predigestion volume with DI water in the digestion vessel.

h. When necessary, filter or centrifuge the sample to remove insoluble material that could clog the nebulizer. The filtering apparatus must be thoroughly cleaned with dilute nitric acid prior to filtration.

i. The sample is now ready for analysis.

j. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards.

3. Method 3010A, "**Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by ICP Spectroscopy**".

a. Shake sample thoroughly and pour 50 mL of the well-mixed sample into the digestion vessel.

b. Add 1.5 mL concentrated HNO_3 to the sample.

c. Cover the sample with a ribbed watch glass.

d. Transfer the digestion vessel to a pre-heated hot plate or hot block at 90 to 95°C. A temperature blank must be used, with the temperature being recorded in the log book. Take the volume down to a low

volume (~5 mL), **making certain that the sample does not boil. This is extremely important. Boiling may lead to vaporization of certain analytes. Also make certain that no portion of the bottom of the digestion vessel is allowed to go dry. This may lead to low recoveries.** Remove the sample from the hot plate and cool.

e. Add another 1.5 mL portion of concentrated HNO_3 to the sample.

f. Cover the sample with a ribbed watch glass.

g. Transfer the vessel to the hotblock or equivalent source. Increase the temperature so a gentle reflux occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing).

h. Uncover the vessel and evaporate to a low volume (~3 mL) **making certain that no portion of the bottom of the digestion vessel is allowed to go dry.** Remove and cool.

i. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution).

j. Cover the digestion vessel and reflux for an additional 15 minutes.

k. Bring sample to its predigestion volume in digestion vessel.

l. When necessary, filter or centrifuge the sample to remove insoluble material that could clog the nebulizer. The filtering apparatus must be thoroughly cleaned with dilute nitric acid prior to filtration.

Note: When preparing USACE project samples, if any sample in a digestion batch requires filtration, all samples (including QC samples) must be treated in the same manner.

m. The sample is now ready for analysis.

n. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards.

4 Method 3030C (Standard Methods), "**Preliminary treatment for Acid-Extractable Metals**"

a. Shake sample thoroughly and pour 50 mL of the well-mixed sample into a 500 mL digestion vessel.

b. Add 2.5 mL 1:1 HCl to the sample.

c. Heat 15 minutes in a hot bath.

d. Filter through a membrane filter.

e. Adjust filtrate volume to 50 mL with DI water.

f. Transfer to ICP analyst.

D. Solid sample preparation

It is extremely important that waste (when appropriate), soil and sediment samples be mixed thoroughly to ensure that the sample is as representative as possible of the sample media. The most common method of mixing is referred to as quartering. The quartering procedure should be performed as follows:

- *The material in the sample pan(inorganic-plastic/organic-aluminum) should be divided into quarters and each quarter should be mixed individually.*
- *Two quarters should then be mixed to form halves.*
- *The two halves should be mixed to form a homogenous matrix.*

This procedure should be repeated several times until the sample is adequately mixed.

NOTE: Samples that are clay type materials should be handled in a different manner. Due to these type sample matrices having an affinity to stick to most anything that touches it, another approach must be followed. Obtain a representative sub-sample aliquot from the center or middle section of the sample container.

Grinding of Vegetation Samples

Remove sample from shipping container and brush off dirt particles. Chop sample into about half inch pieces with clippers or other cutting tool. Place the sample in an aluminum pan and air-dry in an exhaust hood to the appropriate dryness for grinding. It should be dry enough where it won't stick to the inside of the mill. Grind the dried sample to fineness in either the manual sample mill

or the Wiley mill or both if needed. Place the ground sample in a container and label immediately.

1. USEPA CLP ILM0 4.1, **"Acid digestion of Soil/Sediment"**

   a. Mix the sample thoroughly to achieve homogenity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 1.5 g portion of sample and transfer to a digestion vessel.

   b. Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass or equivalent source. Heat the sample to 92 to 95°C and reflux for 10 minutes without boiling. Allow the sample to cool, add 5.0 mL of concentrated HNO_3, replace with watch glass or equivalent source, as appropriate, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the heating vessel.

   c. After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3.0 mL of 30% hydrogen peroxide (H_2O_2). Return the heating vessel to the hot plate or equivalent heating source for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the heating vessel.

   d. Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2.)

   e. If the sample is being prepared for ICP analysis of Al, As, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Ag, Na, Tl, V, and Zn, add 5 mL of 1:1 HCl and 10 mL of Type II water, return the covered heating vessel to the hot plate or equivelent heating source, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 50 mL with Type II water. NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. Dilute the digestate to 144 mL with DI water, add 5 mLs concentrated HCl and 1 mL of concentrated HNO_3, mix well and place into the appropriate container. The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3. The sample is now ready for analysis.

f. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards and ID of matrix spikes and the amounts used for spiking.

2. Method 3050B, **"Acid digestion of Sediments, Sludges and Soils"**

a. Mix the sample thoroughly for 5 minutes using a plastic spatula or Teflon coated spatula in a glass or plastic weigh boat to achieve homogeneity.

b. Weigh approximately (to the nearest 0.01 g) a 1 to 1.5 g portion of the sample directly into a digestion vessel. For samples with low percent solids a larger sample size may be used as long as digestion is completed. Record the exact mass in the digestion log.

NOTE: To achieve the lowest reporting limit possible, use a 2.0 g portion of sample with an ending volume of 100 mLs.

c. Add 5 mL D.I. water and 5 mL concentrated HNO_3(1:1), mix the slurry and cover with a watch glass. Place the sample in a preheated hot block and reflux at 95°C for 10 to 15 minutes being certain that the sample does not boil. Record temperature in digestion log book

d. Allow the sample to cool. Add 5 mL concentrated HNO_3, replace the watch glass and heat/reflux again for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of concentrated HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a watch glass or equivalent allow the solution to evaporate to approximately 5 mL without boiling at 95°C $\pm$ 5°C for approximately two hours. Maintain a covering of solution over the bottom of the vessel at all times. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker. If the volume does get low, add 2.5 mL of D.I. water to bring volume back up.

e. Take the sample off the hot block and allow it to cool. Next, add 2 mL of D.I. water and 3 mL of 30% Hydrogen Peroxide. (The sample will bubble upon the addition of H_2O_2 if it is still warm.) Cover the vessel with a watch glass and return the sample to the hot block or equivalent source and heat until the bubbling subsides. Care must be taken to

ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker. Add two more 3 mL portions of H_2O_2 to the sample in the same manner as before. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2.)

f. Cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate at 95°C ± 5°C without boiling for approximately two hours until the volume has been reduced to approximately 2.5 mL. Maintain covering of solution over the bottom of the vessel at all times.

g. Add 2.5 mL of DI water and 2.5 mL of concentrated HCl and 10 mL of DI water, cover the sample with a ribbed watch glass and continue refluxing for an additional 10 minutes without boiling

h. When necessary, filter or centrifuge the sample to remove insoluble material that could clog the nebulizer. The filtering apparatus must be thoroughly cleaned with dilute nitric acid prior to filtration.

i. Bring sample up to 50 mL with D.I. water in the vessel. Add 150 ml of DI water to a 250 ml sample bottle. Invert the 50 ml sample digestion vessel several times to mix the sample and pour sample into the 150 ml of the sample bottle. Pour some sample back into the 50 ml sample digestion vessel to rinse and pour back into the 250 ml sample bottle and cap and mix.

NOTE1: When preparing USACE project samples, if any sample in a digestion batch requires filtration , all samples (including QC samples) must be treated in the same manner.

NOTE2: To achieve the lowest reporting limit possible use 2.0 grams of sample with an ending volume of 100 mLs.

j. The sample is now ready for analysis.

k. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards.

E. Oils

1. Method 3031, "**Digestion Procedure for Oils**"

NOTE: THIS METHOD IS VERY TIME CONSUMING--DISCUSS SUB-CONTRACTING SAMPLES WITH YOUR SUPERVISOR AS SOON AS THEY COME IN THE DOOR.

a. Homogenize sample and Weigh approximately (to the nearest 0.01 g) a 0.5 g representative portion of the sample into a 250 mL beaker. Separate and weigh proportional aliquots of the phases if more than one phase is present. Record the exact mass in the digestion log. Larger or smaller sample sizes can be used if needed.

g. Add 0.5 g of potassium permanganate powder. If larger sample sizes are used, increase the amount of potassium permanganate so that the ratio of oil to postassium permanganate is still 1:1. Mix the oil and permanganate thoroughly until homogenous. Thick oils and tars that cannot be mixed should be heated to achieve mixing (the oil may react mildly). It is important to record the amount of potassium permanganate used for each sample if analysis is by ICP-AES and correction is to be made for the amount of manganese. If more than 10% of the sample is aromatic material, such as xylene, then the reaction will be incomplete. If this is the case, increase the amount of potassium permanganate. If the sample is a mixture of oil and other non-organic materials, reduce the amount of potassium permanganate.

NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. This should include face shields and latex gloves.

h. Cautiously add 1.0 mL concentrated H_2SO_4, and stir with an appropriate stirring device. If larger sample sizes are used, increase the volume of the sulfuric acid so that the ratio of oil to sulfuric acid is 1 g to 2 mL. The H_2SO_4 can be added dropwise or all at once, depending on analytical needs. (Generally, dropwise is preferred when low reporting limits are needed.)

NOTE: To prevent a strong exothermic reaction, H_2SO_4 should be added dropwise to all samples unfamiliar to the analyst and to all samples that are known to be highly reactive.

The reaction can take several seconds to begin, but when it occurs it will be very quick, vigorous, and exothermic. Generally larger sample sizes will react faster than smaller. Likewise, lower average molecular weight materials will react faster than heavier. Do not be mislead by an initial lack of reactivity. A grey-white vapor will be ejected from the beaker (SO_3) and splattering and bubbling can occur. The beaker will become very hot. This step is complete when no more gases are given off and the sample would be a thick black lumpy paste. Allow the beaker to cool as needed.

NOTE: Care must be taken when working with very light organic materials, such as diesel fuels, as they may flash. Generally, the lower the average molecular weight of the meterial correlates to a greater danger of flashing. The danger of flashing is reduced by adding the sulfuric acid dropwise.

NOTE: If more than 10% of the sample is aromatic material, such as xylene, only a little grey-white vapor will form. This will reduce accuracy and complicate nebulization. If there is a signigicant amount of non-hydrocarbon material, a sputtering recation will occur and black MnO_2 particulates will be given off. See section (b.) above under procedure.

i. Add 2 mL of concentrated HNO_3 and stir. This reaction will be slightly exothermic. If larger sample sizes are used, it is not always necessary to increase the volume of HNO_3 proportionately, depending on analytical needs. Some reddish-brown vapor (NO_2) may be given off. Allow the reaction to continue until complete, that is when the digestate no longer gives off fumes. Allow the beaker to cool as needed.

j. Add 10 mL of concentrated HCl and str. If larger sample sizes are used, it is not always necessary to increase the volume of HCl proportionately, depending on analytical needs. This reaction will be slightly exothermic and gas formation and foaming will occur. Lighter oils will foam more than will heavier oils. If excess foaming occurs, add water to prevent sample loss. Allow the beaker to cool as needed.

k. Heat the beaker until there is no further gas evolution. (temperature should not exceed 150 °C to prevent volatilization). There may be additional foaming or other milder reactions which may result in overflow from the beaker. If excess foaming occurs, either remove the beaker from the heating source until foaming subsides or add sufficient

water to prevent overflow. The final digestate should be a clear yellow liquid with black or dark reddish-brown particulates.

l. Filter the digestate through Whatman 41 filter paper and collect filtrate in a volumetric flask or beaker.

m. Wash the digestion beaker and filter paper, while still in the funnel, with no more than 5 mL of hot HCl.

NOTE: The purpose of this next step is to recover antimony, barium, and silver that may not have been completely solubilized. If the sample is not being prepared for these analytes, the next step may be skipped.

n. (Optional) After having washed the filter paper, remove the filter and residue from the funnel and place it back in the beaker. Add 5 mL of conc. HCl and place the beaker back on the heating source until the filter paper dissolves (temperature should not exceed 150 °C ±5 °C to prevent volatilization). Remove the beaker from the heating source and wash the cover and sides with reagent grade water and then filter the residue and collect the filtrate in the same flask or beaker as in sections f. and g. above. Allow the filtrate to cool and quantitatively transfer to a volumetric flask. Bring to volume.

o. (Optional) If the filtrate is collected in a beaker, the filtrate can be heated again to drive off excess HCl. This can reduce matrix effects in sample introduction (temperature should not exceed 150 °C ± 5 °C to prevent volatilization). When sufficient HCl has been removed, remove the beaker from the heating source, allow to cool, and then transfer the contents to a volumetric flask and bring to volume. However, if too much HCl is removed, barium, silver and antimony can be lost.

p. Analyze the flitrate by ICP-AES. Depending on the final volume selected, the total solids in the digestate may be high enough to cause nebulization problems. Problems due to high dissolved solids may be corrected by 1) following optional Section i., 2) using internal standards, 3) using flow injection analysis, or 4) using other matrix correction procedures.

Manganese Removal Steps

NOTE: The purpose of these next steps is to remove the manganese in the digest by precipitating it as manganese ammonium phosphate

under alkaline conditions. Elements that do not form insoluble phosphates, such as arsenic, are filtered out and can be analyzed at lower concentrations.

q. Take the digestate, or portion of digestate and reduce the volume to remove as much HCl as possible without going below 10 mL. Then add conc. NH_4OH until pH is 7 or greater. For most matrices, the digestate will change colors (often from yellow to brown) at pH 7. A mild exothermic reaction will occur immediately.

r. Add at least 2 g ammonium phosphate for each 1 g of potassium permanganate used in the digestion and stir. An excess of phosphate is needed for good analyte recovery. Then add enough water and mix to ensure maxium precipitation. A pink or yellow silky amorphous precipitate, manganese ammounium phosphate, will form. If too much NH_4OH is used some of the manganese ammonium phosphate can be solubilized. Stir until precipitation is complete. Some ammonium phosphate may remain unreacted at the bottom of the beaker.

s. Filter the digestate through Whatman 41 filter paper (or equivalent) and collect filtrate in a volumetric flask or beaker.

t. Heat the filtrate to volatilize the ammonia (temperature should not exceed 150 °C ± 5 °C to prevent volatilization). The volume of filtrate can be reduced by heating to no less thatn 10 mL. If too much water is removed ay ammonium chloride formed will solidify. If this occurs, either add enough water to dissolve the solids or filter out the solids and wash the residue with deionized water. The filtrate can be analyzed by ICP-AES.

u. The digestion log must contain the date, analyst, sample number, client, sample mass/volume, final volume of digestate, lot # of acids used and the preparation and ID of standards.

X. CALCULATIONS

A. The analyst must be supplied with both beginning sample masses/volumes and final digestate volumes. This information must be recorded in the digestion log.

XI. QUALITY CONTROL

A. Digestion

1. Temperature blank

   a. The temperature of the hot plate/hot block must be monitored for temperature during the digestion process.

   b. The thermometer must be tagged with annual calibration information. Record the thermometer reading, correction factor and the corrected temperature in the digestion log.

2. Blanks

   a. Digest a blank with every batch of samples digested (20 sample maximum). The blank is prepared by adding all the same reagents added to the samples to a clean dry beaker and taking it through the same process as the samples. **NOTE: The blank for OILs MUST include an analyte-free oil or explosive reactions can occur.**

   b. Also, there must be a blank for every different method of digestion that is set up that day, every 20 samples.

   c. There must also be a blank for every different matrix of samples that is to be digested, every 20 samples.

   d. Sample is given a unique identifier in the digestion log.

3. Laboratory Control Samples

   a. For water samples, one LCS is digested with every batch of samples digested (20 sample maximum).

   b. For water samples, a LCS is digested every day for each type of digestion, every 20 samples.

   c. For soil/sediment samples, a soil matrix standard reference material (SRM) must be digested per batch (20 samples maximum) or alternatively a spiked teflon chip sample.

   d. Sample is given a unique identifier in the digestion log.

   e. Recoveries of standard reference materials or laboratory control samples spiked with organo-metallic standards recoveries should be **±25% of their true values for OILS.**

4. Duplicates

   a. A duplicate is prepared every 20 samples. This usually takes the form of a matrix spike duplicate.

      NOTE: Certain projects require a sample duplicate and a matrix spike duplicate with each set of twenty samples.

5. Blank Spike

   a. This is required for certain projects.

B. Sample Matrix

   NOTE: Field blanks/duplicates, trip blanks, or equipment blanks are not to be used for sample matrix QC samples.

   1. Matrix spike

      a. Digest a spike and spike duplicate every 20 samples where sample volume is adequate to do so. Choose a sample (if possible) that has a lot of metals requested to be analyzed.

         NOTE: For some projects, a sample duplicate and sample spike may be required instead of a spike and spike duplicate. Your supervisor should make you aware of these projects.

      b. The following metals do not get digested spikes when using CLP spike.

         Calcium
         Magnesium
         Sodium
         Potassium

      v. For TCLP samples, a spike must be digested for every matrix. You should inspect the sample (original sample prior to extraction) or check the log book to determine matrix type. (Also the matrix spike aliquot must be added to the extract after filtration but before preservation.)

      d. The CLH project requires that a high and a low spike be prepared and analyzed. Spikes shoud be prepared at 40 mg/Kg and 400 mg/Kg for soil samples and 200 ug/L and 2000 ug/L for aqueous samples.

XII. CORRECTIVE ACTIONS

A. Sample boils during digestion.

1. Redigest another sample aliquot.

B. Sample goes dry or portion of beaker bottom is exposed due to excess evaporation during digestion.

1. Redigest another sample aliquot.
2. Glass beaker dry for an extended period of time? Discard beaker.

XIII. SPECIAL NOTES

A. **Never** take for granted how a sample should be digested. If the sample looks strange or unusual, or if you are not sure what metals the sample gets, what detection limits are required, whether the sample is total or dissolved, or even what method of digestion should be used, always ask your supervisor or the person who is to analyze the sample. How metals need to be digested changes too often to take it for granted.

B. **Antimony (Sb) soils** should be analyzed within 48 hours of digestion whenever possible. When a soil requesting Antimony analysis is received, you must coordinate with the person who will be analyzing it to be sure that they can analyze it on the same day that it is digested.

C. Labels for the digested sample must be written in a neat and legible manner. The labels must include such information as sample number, client name, the date digested, and the volume or mass digested.

D. There are several precautions that must be taken to minimize the possibility of contamination.

1. All metals glassware must be kept separate from all other laboratory glassware.

2. Metals glassware must be washed as soon as possible after being used. **Dirty metals beakers must not be left overnight.**

3. Acid to be used for metals digestions must be kept separate from all other laboratory acid.

E. Samples must be digested in a timely manner to ensure ICP analysis remains on schedule for data generation. Samples received on or before Wednesday of week X must be prepared for ICP digestion by the end of week X. Your supervisor must be consulted if this schedule can not be met at a particular time.

F. Please consult Waste Disposal SOP-405, for information concerning disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

The following is a list of changes for sample preparation when the 5.2 statement of work is required:

1. Soluble samples are required to be digested unless the chain of custody specifically states that digestion is not required. An MDL study must be done on the unprepared MDL solution in order to provide MDL levels for samples that are not digested. When digestion is not required an LCSW and post digestion spike are not required.

2. Digestates must be stored until 365 days after delivery of a complete, reconciled data package.

3. Preparation codes are used on form 13's. They are found in the 5.2 statement of work page B-39 3.4.12.2.4.

DEFINITIONS – Refer to SOP-431 for common environmental laboratory definitions.

MERCURY ANALYSIS IN SOIL/SEDIMENT BY MANUAL COLD VAPOR TECHNIQUE METHODS SW846 7471A, 245.5 and CLPILM 04.1 (NJDEP does not accept CLPILM 04.1 after June, 2003), Addendum for USEPA CLP ILM 05.2

SOP NUMBER: SOP-104

REVISION NUMBER: 14

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 07/21/06

DATE OF LAST REVIEW 07/21/06

MERCURY ANALYSIS IN SOIL/SEDIMENT BY MANUAL COLD VAPOR TECHNIQUE

References:
SW846 Method 7471A
USEPA Method 245.5, CLP SOW ILM04.1
See Addendum for CLP SOW ILM05.2

I. SCOPE AND APPLICATION:

A This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials.

B. The range of the method is 0.2 to 2 µg/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

II. SUMMARY OF METHOD:

A. A weighed portion of the sample is acid digested for 2 minutes at 95±2°C, followed by oxidation with potassium permanganate and with a secondary digestion at 95°C for 30 minutes. Mercury in the digested sample is then measured by the conventional cold vapor technique.

III. SAMPLE HANDLING AND PRESERVATION:

A. Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the lab that may result in contact with solid, liquid or airborne mercury.

B. Refrigerate solid samples at 4°C (±2°C) upon receipt until digestion and analysis.

C. The sample should be analyzed without drying. A separate percent solids determination is required

D. The holding time for digestion of mercury samples is 28 days.

IV. INTERFERENCES:

A. Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

B. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

C. Samples high in chlorides require additional permanganate (as much as 12.5 mLs) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell.

D. Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

V. SAFETY

A. Normal accepted laboratory practices should be followed while performing this procedure.

B. The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be minimized by good laboratory practices. Normal accepted laboratory safety practices should be followed during reagent preparation and instrument operation. Always wear safety glasses or full-face shield for eye protection when working with these reagents. Each laboratory is responsible for maintaining a current safety plan, a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.

C. Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analyses should be conducted in a laboratory exhaust hood. The analyst should use chemical resistant gloves when handling concentrated mercury standards.

VI. EQUIPMENT/APPARATUS:

A. Perkin Elmer Flow Injection Mercury System (FIMS)

B. Perkin Elmer AS 90

C. Mercury lamp

D. Environmental Express Mod-Block digestion block capable of holding 95±2°C for 2 hours

E. A scale or balance capable of weighing to 0.01 ± 0.02 gram.

F. Snap cap digestion polypropylene vessels for use with the mod block digester. **Five vessels of each lot must be taken through analysis to check for mercury**

G. Polypropylene watch glasses suitable for use with the above vessels in F above.

H. Manual Sample Mill

I. Wiley Sample Mill

J. Clippers for cutting vegetation

VII. REAGENTS AND STANDARD PREPARATION:

A. REAGENTS

1. Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

2. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3. Both HNO_3 and HCl must be of the reagent grade suitable for mercury determinations.

   NOTE: This reagent is required for use when USACE project samples are being digested.

3. Concentrated HCl.

4. Concentrated HNO_3.

5. Stannous chloride in a one liter volumetric flask add ~500 mL D.I. H_2O, 30 mL concentrated HCl, and 11g stannous chloride crystals. Swirl to mix and dilute to 1 L.

6. Sodium chloride-hydroxylamine chloride solution: Dissolve 120 g of sodium chloride and 120 g of hydroxylamine sulfate in reagent water and dilute to 1 L. Note : this is normally made up 2 liters at a time.

7. Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 200 g of potassium permanganate in 4 L of reagent water.

8. 3 % HCl carrier solution: 30 mL HCl – 1 L DI H20; Prepare fresh daily.

9. Potassium persulfate 5% solution: Dissolve 100g in 2 liters of D.I. water. Used with digestion of CLP soils.

B. STANDARDS

1. Traceability

a. A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

b. All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

c. The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

2. Preparation

NOTE: All standard solutions should be prepared using class A volumetric flasks, class A volumetric pipettes (or calibrated Eppendorfs). All Standards, blanks, and samples are taken through the digestion process.

a. Stock mercury solution: (100 µg/mL). Order from manufacturer already prepared. This solution is given a unique identifier.

b. Primary source and secondary source mercury standard solutions: dilute 2 mL of stock solution to 1000 mL in a 1000 mL volumetric flask, with 1.5 mL concentrated HNO_3 (200 ug/L).

c. Calibration standards

i. Prepared from the primary source standard. The preparation of the calibration standards, etc. is described below.

a. Dilute the volumes below to 5 mLs in a 70 mL polypropylene vessel. (Note: The standards are diluted to 5 mLs for the initial step of the digestion.)

ug/L Hg	mLs of 200 ug/L standard in 50 mL
0.20	0.050
0.50	0.125
1.0	0.25
2.0	0.50
4.0	1.0
6.0	1.5
10.0	2.5

ii. Appropriate reagents are added as below in the sample preparation section.

iii. Prepare one vessel of each.

iv. It is necessary to digest the calibration standards when following all mercury methods.

e. Calibration verification standards

i. Initial calibration verification (ICV) solution – 4.0 ug/L

a. Prepared from the secondary source mercury standard (200 ug/L).

b. Prepared by diluting 1.0 mL of the second source mercury standard to 5 mLs in a polypropylene digestion vessel.

c. Appropriate reagents are added as below in the sample preparation section.

d. It is necessary to digest the ICV standards when using all mercury methods for soil.

ii. Continuing calibration verification (CCV) solution

a. Prepared from the primary or secondary source mercury standard. The concentration is alternated from 2.0 ug/L to 4.0 ug/L every 20 samples.

b. Prepared by diluting 0.50 for a 2.0 ug/L and 1.0 mL for a 4.0 ug/L of the secondary 200 ug/L standard to 5.0 mL with reagent water in a polypropylene digestion vessel.

c. Appropriate reagents are added as below in the sample preparation section.

d. It is necessary to digest the CCV standards when following all mercury methods for soil.

f. Digestion standards

1. Laboratory control sample

a. The Laboratory Control Sample (LCS) is prepared from the secondary source mercury standard (200 ug/L) and added to ~ 0.3 grams of teflon chips.

b. Prepared by diluting 0.50 mL of the secondary mercury standard (200 ug/L) to 5 mLs in a polypropylene digestion vessel with 0.30 grams of teflon chips.

c. Appropriate reagents are added as below in the sample preparation section.

d. This solution is given a unique identifier in the digestion log.

2. Matrix Spikes

a. Prepared from the primary or secondary source mercury standard (200 ug/L).

b. Prepared by adding 0.50 mL of the mercury standard (200 ug/L) to the sample in a polypropylene digestion vessel. Project specific requirements may over-ride the spiking level.

c. Appropriate reagents are added as below in the sample preparation section.

VIII. CALIBRATION:

A. Set up the instrument with proper operating parameters.

1. Perkin Elmer Flow Injection Mercury System (FIMS)

a. Prepare the instrument for calibration by the following steps:

i. Replace any old tubing that is around the pump cylinder. The sample transfer tubing connected to the seperator cover must not have any moisture in it. If it does replace it. **(Perkin-Elmer tygon tubing, waste and carrier 1.52mm I.D.,waste only 3.17mm I.D., stannous chloride 1.14mm I.D.)**

ii. Also replace the filter membrane with the rough side up. (for instructions refer to page 1-22 in maintenance manual.)

iii. Turn on PE 100 spectrophotometer; (Note: this must be on in order to start up the software on the computer.)

iv. Turn on computer and go to icon "AA Win LAB Analyst"

v. Go to method; select "Hg CAL 2" then OK.

vi. Wavelength = 253.7; smoothing points =9; measurement = peak height; read time = 18 sec.; BCC time = 2 sec.

vii. Go to "Sample Info" and enter the order of the samples and other information that may be needed.

viii. Save entered sample list under "Save ...sample info file" Note: description and batch ID are normally the date of analysis.

ix. Go to "auto"; then to set-up. Select Browse in both spaces. One is to bring up your saved "Sample Information." File. The other is to select a results library. Double click on heading and choose.

x. Turn the printer on.

xi. Connect all tubing to the pump and blocks.

xii. Start the pump by going to "FIAS" and click the pump 1 Icon (120).

xiii. The pump witll start, then lock down and tighten the tubes onto the pump.

xiv. Turn on the nitrogen tank, it should be >500 psi on the guage. Replace the nitrogen tank when it is at 500 psi.

xv. The pressure gauge on the PE100 should be just below 100.

xvi. Use the tension adjuster to press down the tubing magazine to the pump head on the top and bottom. Start the pump and then lock them down. This technique needs to be demonstrated so

that a new user will be able to understand what is needed here and how to do it.

xvii. Adjust the spring tension tubing until there is a constant "bubble of low rate" coming out to the waste tube.

xviii. Place carrier tubes into carrier and stannous chloride tube into SnCl2. (click valve fill inject and make sure flow is correct and the line is rinsed)

xix. Make sure the permanganate waste bottle is bubbling in order to absorb any Hg vapors which could be vented into the room.

xx. Allow a few minutes for reagents to flow through the system before starting analysis.

xxi. Calibrate: Go to "Auto" click on "Analyze", click on "calibrate".

xxii. "Select location" enter the #'s of the samples to be analyzed, then "OK".

B. Analyze the calibration standards as below.

1. A curve must be analyzed daily for all projects. A new curve must be analyzed when the ICV analysis is not within ±10% for SW846 7471 or ±5% for 245.5 methods.

2. The curve should be linear with a calculated intercept with a minimum correlation coefficient(r) of $\geq$0.995 (USACE) or 0.998 (other). If not, a new curve must be analyzed.

3. **CLP requires a blank + 5 calibration standards (0, .02, .05, .1, .5 and 1.0 µg). (One standard must be at CRDL or IDL whichever is greater.)**

IX. PROCEDURE:

A. Prepare calibration standards as detailed above. Add all reagents to the standards which are added to the samples as outlined below. Record the standard preparation in the standard log.

B. Sample preparation

It is extremely important that waste (when appropriate), soil and sediment samples be mixed thoroughly to ensure that the sample is as representative as possible of the sample media. The most common method of mixing is referred to as quartering. The quartering procedure should be performed as follows:

- The material in the sample pan(inorganic-plastic/organic-aluminum) should be divided into quarters and each quarter should be mixed individually.

- Two quarters should then be mixed to form halves.
- The two halves should be mixed to form a homogenous matrix.

This procedure should be repeated several times until the sample is adequately mixed.

NOTE: Samples that are clay type materials must be handled in a different manner. Due to these type sample matrices having an affinity to stick to most anything that touches it, another approach must be followed. Obtain a representative sub-sample aliquot from the center or middle section of the sample container.

Grinding of Vegetation Samples

Remove sample from shipping container and brush off dirt particles. Chop sample into about half inch pieces with clippers or other cutting tool. Place the sample in an aluminum pan and air-dry in an exhaust hood to the appropriate dryness for grinding. It should be dry enough where it won't stick to the inside of the mill. Grind the dried sample to fineness in either the manual sample mill or the Wiley mill or both if needed. Place the ground sample in a container and label immediately.

1. Transfer 0.30 g (for USACE work use anywhere from 0.20 to 1.0 g and record the weight in the digestion log) of sample to a polypropylene digestion vessel previously marked for this sample. Record the exact sample mass on the bottle and in the digestion log. (Note: the balance must be calibrated for the specific task. Calibrate by weighing a 0.5 and a 0.1g weight on the balance along with a digestion vessel. Record in specific balance calibration log.)

2. Add 2.5 mL of reagent water, and 2.5 mL of aqua regia and mix for samples. Add 2.5 mL of aqua regia to standards and mix.

3. Cover samples and standards with watch glasses and heat for 2 minutes in the hot block at 95$\pm$2°C (The hot block temperature must be monitored and documented. Record observed temperature, correction factor, and the corrected temperature).

4. Cool, bring to 30 ml with D.I. water

5. Add 7.5 mL potassium permanganate solution to each vessel and mix. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate to the solution if necessary, until the purple color persists for at least 15 minutes (not more than 12.5 mL).

NOTE: The same amount of $KMnO_4$ added to the samples should be present in the standards and blanks.

6. Heat for 30 minutes on the hot block at 95±2°C (The temperature must be monitored and documented. Record observed temperature, correction factor, and the corrected temperature), cool. Samples may be saved at this point if there is not time to run the whole set that day.

7. Add 3 mLs of sodium chloride-hydroxylamine chloride solution to each vessel.

8. Bring to 50 ml with D.I. water both standards and samples. Cap mix and vent to decolor and release Cl gas. The samples are now ready for analysis.

NOTE: Stannous Chloride (VII. A 5.) and 3% HCl (VII. A 8.) are added by the instrument during analysis.

C. Sample analysis

1. Set up the instrument as described in the calibration section above.

2. When ready to run samples, transfer samples and standards to autosampler tubes and load the auto sampler according to the sample information sheet set up previously. If chlorides are suspected, purge the head space in the polyethylene tube for at least 1 minute to get rid of any chlorine gas collected there. After a delay of at least 30 seconds the sample is ready for step "3". **NOTE:** When aqua-regia is added assume that all samples and standards have chlorine and treat accordingly. Purging the samples of chlorine is accomplished by putting a pasteur pipette on the end of some air tubing hooked to a fish pump. The pasteur pipette is then placed at an angle into the top of the polyethylene vessel without breaking the surface of the sample. It takes about one minute to purge the air above the sample of chlorine.

3. Analysis must be preceded by the analysis of an ICV (concentration at or near mid range) with control limits of ±10% for SW846-7471A and ±5% for 245.5 methods.

4. The ICB must follow the calibration standards (<±MDL (USACE) or ±RL/CRDL for other or CLP), but not before the ICV. **No analyte must be detected > 2xMDL for DOD QSM Ver. 3.**

5. Each set of ten samples must be followed by a CCV with control limits of ±20% for SW846-7471 and ±10% for 245.5 method. The run must also end with a CCV, then CCB.

6. Analyze CCB after calibration and each CCV. The CCB frequency is 10% or every 2 hours whichever is more frequent. (control limit is < ±MDL or ±RL/CRDL for other or CLP). **For DOD QSM Ver.3 CCB at beginning and end of sequence and after every 10 samples. No analyte detected > 2xMDL.**

7. Instrument Run Log example:

AS LOC	Sample ID
0	Wash
1	0.0
2	0.O2
3	0.05
4	0.1
AS LOC	**Sample ID**
5	0.2
6	0.4
7	0.6
8	1.0
9	ICV
10	ICB
11	LCSW
12	PBW
13	Sample
14	Sample
15	Sample
16	Sample
17	Sample
18	Sample
19	Sample
20	Sample
21	CCV
22	CCB
23	Sample
24	Sample
25	Sample
26	Sample
27	Sample
28	Sample
29	Sample
30	Sample
31	MS
32	MSD
33	FCV
34	FCB

8. Sample analysis:

   i. Go to "Analyze", "select location" and type in the range of numbers needed to complete analysis. (ie. 9-54). Press enter and the autosampler will proceed to enter the selected range. NOTE: Check standards are loaded as part of the tray.

   ii. Make sure that the sample wash beaker is filled with 3% HCl.

   iii. Dilute and reanalyze samples that are more concentrated than within 10% of the high standard. Soil sample dilutions are made from the digested aliquot. Sample concentration results that are below the calibration curve but above the MDL are reported flagged as estimated, ("B" flag).

D. Data reporting

1. Reduce data to result which will be reported using the soil spreadsheet found on the network..

2. Complete the data review checklist (attached). Must be completed and attached to each set of USACE data.

X. CALCULATIONS:

A. Pull up the blank spreadsheet at K:\wcm\tests\mercury and fill in all the information pertinent to the current analysis. Save as the date of analysis. This information can be obtained from your mercury digestion log.

B. Input the sample absorbance into the excel spreadsheet in the appropriate cell. The spreadsheet uses the current calibration to calculate the Hg results.

C. Make sure that the appropriate dilution factors are entered into the spreadsheet in the correct cells.

D. The spreadsheet should divide the result which is the µg Hg obtained from the sample mass by the sample mass in grams. This will yield a result of µg Hg/g sample on a wet weight basis. Calculations in the spreadsheet should be checked occassionally to make sure that they are working correctly.

E. If available, divide the result by the %solids to obtain the result on a dry weight basis.

F. Report the data as µg Hg/g of sample (mg/kg wet or mg/kg dry when % solids are available).

XI. QUALITY CONTROL (Reference SW-846, 7471A Update III, USEPA CLP ILMO 4.1 or EPA 245.5 for further clarification)

A. Daily

1. **The instrument must be calibrated daily for all projects.**

2. Begin each analysis with an ICV. The control limits are ±10% for 7471 and ±5% for 245.5.

3. Analyze ICB. Control limit is **<± MDL** or ±RL/CRDL for other or CLP. **For DOD QSM Ver. 3, no analyte detected > 2x MDL.**
4. If the ICV is not in control a new curve must be analyzed prior to sample analysis.

5. Follow each set of 10 samples with a CCV and also must end up with CCV after last sample. The control limits are ±20% for SW846-7471 and ±10%for 245.5. If an exceedance occurs, analyze another CCV, if the second CCV fails, then a new calibration curve should be generated and all affected samples should be reanalyzed.

6. Follow each CCV with a CCB. Control limit is **< ±MDL** or ±RL/CRDL for others or CLP. **For DOD QSM Ver. 3, no analyte detected > 2x MDL.**

B. Quarterly

1. IDLs for CLP (Follow SOP - 414).

C. Annually

1. MDLs must be analyzed for all matrixes (Follow SOP - 414).

D. Digestion

1. LCS data should be maintained and available for easy reference or inspection.

2. Preparation blank (< ±½ RL or ±RL for common contaminates or ±RL/CRDL for others or CLP)

a. Employ a minimum of one preparation blank per sample batch to determine if contamination or any memory effects are occurring. The preparation blank is taken through the same digestion/preparation steps as the samples being tested. The result for the preparation blank must be < ± ½ RL for USACE or ±RL/CRDL for others or CLP. If not, the analyst must use good judgment to evaluate the impact upon the associated samples. There is no impact if an associated sample is below the method detection limit or if the level in the sample is greater than 10X the level found in the preparation blank. If the level of mercury in a sample is above the method detection limit, but less than 10X the level found in the preparation blank, the sample must be redigested and reanalyzed or the data must be qualified on the final report. The project manager or QA officer will make this determination.

3. Laboratory control sample (LCS).

a. Employ a minimum of one LCS per sample batch to verify the digestion procedure.. The LCS is taken through the same digestion/preparation steps as the samples being tested. The minimum control limits are ±20% for SW846-7471 and ±15% for 245.5 solid samples. An LCS will accompany each batch of soil samples. If the LCS is not in control, the Inorganic Manager and QA Officer must be notified immediately. Several possibilities exist at this point and a thorough investigation and data evaluation is essential. The first question is to evaluate the impact upon the data. All samples may need to be retested or flagged with the appropriate qualifier. The next question is to find out why it occurred and to proceed with a corrective action plan to prevent reoccurrence. This corrective action is documented in a CAR.

E. Sample matrix

1. Analyze one replicate sample for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. It is acceptable to substitute a matrix spike duplicate for the sample replicate. Project specific requirements will take precedence in these situations.

2. Analyze one spiked sample and spiked sample duplicate for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. Project specific requirements will take precedence in these situations. CLP requires 1 duplicate and 1 spike per batch. If the analyte level in the sample is not greater than four times the

spiking level, the spike recoveries should be within ±25% of the true value. If results do not fall within the control limit-redigestion/reanalysis may be required. If reanalysis is not required, the associated batch of samples will be flagged accordingly. Discuss the situation with your supervisor. A Corrective Action Report (CAR) must be filled out and attached to the data as well as emailed or sent to the supervisor when the control limits are exceeded.

3. The relative percent difference (RPD) between replicate determinations is to be calculated as referenced in the laboratory QA manual. (A control limit of ± 20% RPD (non-aqueous samples may routinely exceed this amount) shall be used for sample values greater than ten times the instrument detection limit.) Supervisor must be notified if the control limit is not met. Supervisor will determine corrective action if required. The final analytical report must document this situation. A Corrective Action Report (CAR) must be filled out and attached to the data as well as emailed or sent to the supervisor when the control limits are exceeded.

4. For 245.5 analyze one serial dilution (1 to 5 dilution) for every 20 samples or per analytical batch, whichever is more frequent. Percent recovery should be 10%. The concentration of the original sample should be a minimum of 50X the IDL in order to apply the recovery criterion; if not, the serial dilution approach is not used.

5. Criteria for Arizona samples: A dilution check of one sample per batch must be performed and required to be within ±10%. If this limit is exceeded or if the batch contains only non-detects, then the analyst must perform a post-digestion spike, which must be within ±15%. If this limit is not met, all samples in the batch must be analyzed by the MSA.

6. When the sample matrix is so complex that viscosity, surface tension, and components can not be accurately matched with standards, the method of standard addition (MSA) is recommended. Section 8.6 of SW846-7000A provides tests to evaluate the need for using the MSA.

F. Method Detection Limit (MDL), Empirical Laboratories' Reporting Limit (ERL), Contract Required Quantitation Limit (CRQL) and Analyte Wavelength:

TABLE I

Solid/Soil Method Detection Limits(MDL), Empirical Laboratories' Reporting Limits(ERL), CLP OLM04.1 & OLM05.2 Contract Required Quantitation Limits (CRQL)				
Mercury by EPA	**SOLID/SOIL**	**SOLID/SOIL**	**SOLID/SOIL**	**SOLID/SOIL**

245.1, 245.5, 7471A, SOW 4.1 & 5.2	MDL (mg/Kg)	ERL (mg/Kg)	CRQL ILMO 4.1 (mg/Kg)	CRQL ILMO 5.2 (mg/Kg)
Mercury	0.0157	0.033	0.1	0.1

TABLE 2

ANALYTE	WAVELENGTH
Mercury	**253.7**

XII. CORRECTIVE ACTIONS

A. INSTRUMENT RELATED

1. ICV not within ± 10% (SW846) or ± 5% (245.5)
   a. If the problem is with the solution.
      i. Reprepare, obtain new stock if necessary.
   b. If the problem is with the calibration.
      i. Recalibrate thru analysis of appropriate standards and recheck ICV.

2. CCV not within ± 20% (SW846) or ±10% (245.5)
   a. If the problem is with the solution.
      i. Reprepare, obtain new stock if necessary.
   b. If the problem is with the calibration.
      i. Recalibrate thru analysis of appropriate standards and reprepare/reanalyze the previous ten sample according the following guidelines.
         a. If the CCV was biased high, any of the previous ten samples which were below the minimum detection limit do not require reanalysis.
         b. If the CCV was biased low, the previous ten samples must be reanalysed.

B. DIGESTION RELATED

1. The preparation blank less than ± ½ RL for USACE or ±RL/CRDL for others or CLP.
   a. If the problem is with the instrument or stannous chloride.
      i. Analyze a reagent blank to determine the stannous chloride and the instrument are behaving properly. If this check has detectable mercury, reprepare the stannous chloride or determine if there are any problems with the instrument.

ii. If the problem was with the instrument or the stannous chloride and the situation is corrected continue analysis with a second aliquot of the preparation blank.

b. If the problem is with the digestion.

i. All associated samples which are below the method detection limit (MDL) or have a level of mercury greater than 10X the level found in the preparation blank can be reported. If the level of mercury in an associated sample is not <MDL nor greater than 10X the level found in the preparation blank, the sample must be redigested/reanalyzed or reported as qualified. The project manager or QA manager will make this determination.

2. LCS not within control limits.

a. If the problem is with the instrument.

i. Reanalyze when instrument is in control with another aliquot of the sample.

b. If the problem is with the digestion.

i. If biased low, associated samples must be redigested.

ii. If biased high, the impact upon the data user must be evaluated. The samples will be redigested or the data will be qualified on the final report.

C. SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20%

i. The associated sample data must be qualified on the final report.

2. Spike analysis recovery not within ±25%

i. If the analyte level in the sample is greater than 4X the spiking level, the %recovery can not be evaluated and no action is taken.

ii. If the analyte level in the sample is not greater than 4X the spiking level, the associated sample data must be qualified on the final report. A corrective action report must accompany the data and be emailed or given to the superviser.

XIII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area.

Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIV. REFERENCES

1. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846; Third Edition (Update III)*; Method 7471A

2. USEPA *Code of Federal Requlations, 40, CH 1,PT 136;* Method 245.1; APX-B

3. USEPA *Contract Laboratory Program(CLP) for Inorganics ILM04.1; ILM05.2*

XV. DEFINITIONS

1. Refer to SOP-431 for common definitions.

Addendum for USEPA CLP ILM 05.2

1. CCV concentration must be different from ICV.

2. The same CCV shall be used throughout analysis for a sample delivery group.

3. Calibration standards must be within 5% of the standard concentration.

4. 0.2 grams of sample must be used for the sample aliquot, add enough reagent water to each sample to make a total volume of 10 mL. Proceed with method as in the water method SOP 103.0 Revision 9.

5. The ICV and CCV must be at ±20% recovery.

6. A CRA must be analyzed at the beginning and end of each batch of 20 samples. Right after the ICV/ICB and right before the final CCV/CCB. The control limit is ±30%.

7. The matrix spike must be analyzed at the concentration of 0.5 mg/Kg.

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):
Batch Number(s):
Method: 7471A (Mercury)

QA/QC Item	Yes	No	NA	Second Level Review
1. Were samples analyzed within USACE holding times?				
2. Was initial calibration curve QC criteria met?				
3. Was all continuing calibration criteria in control?				
4. Did any sample exceed the highest calibration standard? (If yes, were appropriate dilutions made to generate samples concentration within calibration range?)				
5. Did LCS or blank spike meet control limits?				
6. Did MS/MSD meet control limits?				
7. Was the preparation (Method) Blank below the project required detection limits?				
8. Did you return samples back to cold storage immediately after use?				
9. Was water bath temperature monitored/documented and did you apply the thermometer correction factor?				
10. Sample preparation information is correct and complete.				
11. Analytical results are correct and complete.				
12. The appropriate SOP's have been used and followed.				
14. "Raw data" including all manual integration's have been correctly interpreted.				
15. "Special" sample preparation and analytical requirements have been met.				
16. Documentation complete (e.g., all anomalies in the analytical sequence have been documented, corrective action forms are complete.				

ANALYST DATA REVIEW CHECKLIST
7471A (Mercury)

Comments on any "No" response:

_____

_____

_____

_____

_____

_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

METALS ANALYSIS

BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY (ICP-AES) TECHNIQUE

METHODS 200.7, (SW846) 6010B, (SM 19th Edition 2340B) Hardness Calculation, (USEPA CLP) ILMO 4.1 (NJDEP does not accept CLPILM 04.1 after June, 2003)

Addendum for USEPA CLPILM 05.2

SOP NUMBER: SOP-105

REVISION NUMBER: 12

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 07/24/06

DATE OF LAST REVIEW: 07/24/06

ICP METHOD
SOP
References: SW-846, Method 6010B, December 1996
USEPA, Method 200.7, June 1991, Standard Methods 19th Edition 2340B, 1995
USEPA CLP, ILM 04.1. See Addendum for USEPA CLPILM 05.2

I. SCOPE AND APPLICATION

A. Inductively Coupled Argon Plasma (ICP) determines trace elements in solution. **We use the ICP to determine the concentration of the following metals: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, V and Zn.** All matrices, including ground water, aqueous samples, TCLP, SPLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

B. **Detection limits, sensitivity, and optimum ranges of the metals may be found in the ICP method file.** Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

II. SUMMARY OF METHOD

A. Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g., Methods 3005-3050 and SOW ILM 04.1/05.2). When analyzing for dissolved constituents, acid digestion is not always necessary if the samples are filtered and acid preserved prior to analysis. If particulates form after filtration and preservation the sample must be digested prior to analysis.

NOTE: When selenium is required soluble samples must always be digested.

B. This method describes the simultaneous multi-elemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analytic wavelength measured. Background correction is not required in cases of line

broadening where a background correction measurement would actually degrade the analytical result.

C. ICP's primary advantage is that it allows simultaneous determination of any elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and background correction to minimize these interferences, analysis for traces of metals in the presence of a large excess of a single metal is difficult. Examples would be traces of metals in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FAA.

D. It is standard procedure to use an internal standard (Yttrium) with samples to increase the stability of the instrument as recommended by the manufacturer (TJA). (When samples are suspected of containing Yttrium internal standard cannot be used.)

III. SAMPLE HANDLING AND PRESERVATION

A. Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Water samples which have been prefiltered and acidified will not need acid digestion as long as the samples and standards are matrix matched and particulates do not form after the filtration and preservation take place. Solubilization and digestion procedures are presented in Sample Preparation Methods (Methods 3005A-3050A).

B. Sample digestates are stored at room temperature for at least 2 months unless a longer time is requested by the client. The samples contain an acid matrix of 3:1. Since the most concentrated acid matrix allowed for direct disposal down an acid sink is a ratio of 20:1, the samples must be diluted with 1 part water to 2 parts sample prior to pouring down the sink while the tap water is running.

C. **The appropriate SOPs should be consulted regarding sample preparation.** The following is a brief summary of the methods we use for metals preparation.

- Method 3005A prepares groundwater and surface water samples for total recoverable and dissolved metals determination by ICP. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

- Method 3010A prepares waste samples for total metal determination by ICP. The samples are vigorously digested with a mixture of nitric acid and hydrochloric acid followed by dilution with laboratory water. The method is applicable to aqueous samples, TCLP and mobility-procedure extracts.

- Method 3031 prepares oily waste samples for total metal determination by ICP. The samples are mixed with permanganate, H_2SO_4, HNO_3, and HCl, then filtered. The filter is then added back to the filtrate and heated with more HNO_3 and filtered once again. If manganese is needed a manganese removal step is necessary.

- Method 3050B prepares waste samples for total metals determination by ICP. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either laboratory water or hydrochloric acid and laboratory water. The method is applicable to soils, sludges, and solid waste samples.

IV. INTERFERENCES

A. Spectral interferences are caused by background contribution from continuum or recombination phenomena, stray light from the line emission of high-concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

1. Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by measured emission on only one side. The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line interferences are handled by including spectra on interfering species in the algorithm.

2. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If

a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral intereference effects from all method anlytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be done using anlyte concentrations that will adequtetely describe the interfernce. Normally, 100 mg/L single element solutions are sufficient; however, for analytes such as iron that may be found at high concentration , a more appropriate test would be to use a concentration near the upper analytical range limit.

3. Spectral overlaps may be avoided by using an alternate wavelength or can be compensated by equations that correct for interelement contributions. Instruments that use equations for interelement correction require the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive determinations and be reported as analyte concentrations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users may apply interelement correction equations determined on their instruments with tested concentration ranges to compensate (off line or on line) for the effects of interfering elements. Some potential spectral interferences observed for the recommended wavelength are listed in the method in table 2. For multivariate methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

4. When using interelement correction equations, the interference may be expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2 from the method, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximatley 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interferences than that shown in Table 2 from the method. The interference effects must be evaluated for each individual instrument since the intensities will vary.

5. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the entrance and exit slit widths, and by the order of

dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point whre an intefering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.

6. The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and agron flow rate). When using the recommended wavelengths, the anlaylst is required to determine and document for each wavelength the effect from referenced interferences as well as any other suspected interferences that may be specific to the instrument of matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

7. If the correction routine is operating properly, the determined, apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and divided by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adquate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

8. When interelement corrections are applied, their accuracy should be verified, daily, by analyzing spectral interference check solutions. If the correction factors or multivariate correction matrices tested on a daily basis are found to be within 20% criteria for 5 consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such they do not contain concentrations of the interfering elements at ± one reporting limit from zero, daily verification is not required. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change, such as in the torch, nebulizer, injector, or plasma conditions occurs. Standard solution should e

inspected to ensure that there is no contamination that may be perceived as a spectral interference.

B. Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump, by using an internal standard or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, using a high solids nebulizer or diluting the sample. Also is has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance: this may be accomplished with the use of mass flow controllers.

C. Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the elements and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted. Until the required rinse time is established, this method suggests a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon their DQOs.

D. Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the interference check solution with the elements of interest at 0.5 to 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

V. SAFETY

A. Normal accepted laboratory safety practices should be followed while performing this analysis.

1. Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of appropriate safety gloves and lab coats is highly recommended.
2. Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples that need special consideration have applicable notes on the sample logs.
3. MSDS sheets are available for all reagents and standards that have been purchased. These are located in the bookshelves in the Quality Assurance Officers office.

VI. EQUIPMENT/APPARATUS

A. Inductively coupled argon plasma emission spectrometer: Thermo Jarrell Ashe(TJA) 61E trace or equivalent.

B. Computer-controlled emission spectrometer with background correction: Thermo Jarrell Ashe (TJA) 61E trace or equivalent.

C. Radio frequency generator compliant with FCC regulations: TJA 61E trace or equivalent.

D. Argon gas supply – Liquid Argon

E. Class A volumetric flasks

F. Class A volumetric pipettes

G. Analytical balance - capable of accurate measurement to a minimum of three significant figures (.001gm): Mettler model AE100

H. Variable Eppendorf Pipettes 1000µL; 5000µL

VII. REAGENTS AND STANDARD PREPARATION

A. Notes

1. Reagent Water. All references to water in the method refer to reagent grade water unless otherwise specified. Reagent water will be interference free.

2. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

B. REAGENTS

1. Hydrochloric acid (concentrated), HCl.
2. Nitric acid (concentrated), HNO_3.

C. STANDARDS

1. Matrix

a. All standards contain 2% HNO_3 and 5% HCl.

2. Storage

a. The standards are stored at room temperature in 500 mL Teflon bottles.

3. Traceability

a. A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

b. All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date and the logbook where information is recorded. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.)

shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

c. The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

4. Calibration standards

a. All standards have an acid matrix of 2% HNO_3 and 5% HCl and should be prepared using class A volumetric flasks, class A volumetric pipettes (or calibrated Eppendorfs).

b. STD-1 is the calibration blank: Reagent grade water **matrix matched as in (a) above. Note: when this standard is analyzed the intensities should be compared to a previous run to make sure that no contamination has occurred. Prepare this solution fresh daily.**

c. Stock QC21 solution: (100 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier and includes the following metals - Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, Se, Sr, Tl, Ti, V, and Zn.

d. Stock Boron solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

e. Stock Tin solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

d. QC21 High (10 ug/mL). Dilute 50 mL of stock QC21 solution, 5 mL of stock Boron solution and 500 uL of stock Tin solution to 500 mL in a 500 mL volumetric flask, with 25 mL TRACE, Concentrated HCl and 10 mL TRACE, Concentrated HNO3. Prepare this solution fresh every three to six months.This standard is used to calibrate the following-As,B,Be,Cd,Co,Cr,Cu,Mn,Mo,Ni,Pb,Sb,Se,Sn,Ti,Tl,V,Zn.

e. Stock Silver solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

f. Stock Aluminum solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

g. Stock Calcium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

h. Stock Magnesium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

i. Stock Iron solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

j. Stock Potassium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

k. Stock Barium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

l. Stock Sodium solution: (10000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

m. NAK High solution: (500000 ug/L Al,Fe), (2000 ug/L Ag), (5000 ug/L Ba), (500 mg/L Mg). Dilute 25 mL stock Al, Fe, Mg; and 1 ml stock Ag solution; and 0.25 mL of stock Ba solution to 500 mL in a 500 mL volumetric flask with 25 mL TRACE, Concentrated HCl and 10 mL TRACE, Concentrated HNO3. Solution is stable for 6 months.

n. NAK 100ppm solution: (100 mg/L Ca, Na, K.) Dilute 5.0 mL stock Ca, Na, K solutions into a 500ml flask with 25 mL TRACE, Concentrated HCl and 10 mL TRACE, Concentrated HNO3. Solution is stable for 6 months.

o. Stock Arsenic solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

p. Stock Cobalt solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

q. Stock Chromium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

r. Stock Copper solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

s. Stock Manganese solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

t. Stock Nickel solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

u. Stock Lead solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

v. Stock Selenium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

w. Stock Thallium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

x. Stock Beryllium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

y. Stock Cadmium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

z. Stock Antimony solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

aa. Stock Molybdenum solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

bb. Stock Strontium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

cc. Stock Titanium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

dd. Stock Vanadium solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

ee. Stock Zinc solution: (1000 ug/mL). Order from the manufacturer already prepared. This solution is given a unique identifier.

ff. Stock Ultimate Low Standard: (200 µg/L Ag, As, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl); (2500 µg/L Al); (2000 µg/L Fe); (50 µg/L Be, Cd); (10 mg/L B, Sn, Ca, Mg); (500 µg/L Sb, Zn); (1000 µg/L Mo, Sr, Ba, Ti); (200 µg/L V). Dilute 100 uL of stock Ag, As, Co, Cr, Cu, Mn, Ni, Pb, Se, V and Tl solutions; 125 µ/L of stock Al solution; 100 uL of stock

Fe solution; 5 mL of stock B solution; 500 uL of stock Sn, Ca, and Mg solutions; 250 uL of stock Sb and Zn solutions; 500 uL of stock Mo, Sr, Ba and Ti solutions; 1.0 mL of stock Cd and Be diluted to 100 mL and then use 2.5 mL of that solution diluted to 500 mL in a 500 mL volumetric flask with 25 mL TRACE, Concentrated HCl and 10 mL TRACE, Concentrated HNO3. Solution is stable for 6 months.

gg. Ultimate Low Standard: (20 µg/L Ag, As, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl); (250 µg/L Al); (200 µg/L Fe); (5.0 µg/L Be, Cd); (1.0 mg/L B, Sn, Ca, Mg); (50 µg/L Sb, Zn); (100 µg/L Mn, Sr, Ba, Ti); (20 µg/L V). Dilute 10 mL of Stock Ultimate Low Standard to 100 mL in a 100 mL volumetric flask with 5 mL of TRACE, Concentrated HCl and 2 mL TRACE, Concentrated HNO3. This solution is prepared daily.

Stock Ultimate Low Standard and Ultimate Low Standard are only used when specified by client.

5. Calibration Verification standards

a. ICV Prep- 1.0 ml of QC-23, 1.0 ml of QC-7, 0.1 ml of 10,000 ppm Na, 0.09 ml of Fe at 10,000 ppm, and 0.09 ml of Al at 10,000 ppm diluted to 100 ml with 2% HNO3 and 5% HCL matrix. Mix well. CCV Prep- 1.0 ml of QC-21, 1.0 ml of QC-7, 1.0 ml of SN at 100 ppm, 0.1 ml of Na at 10,000 ppm, 0.09 ml of FE at 10,000 ppm,and 0.09 ml of Al at 10,000 ppm diluted to 100 ml with 2% HNO3 and 5% HCL matrix and mix well. This solution is prepared daily. These solutions are given a unique identifier and recorded in the standard log. ICV is prepared from a source independent from that used in the initial calibration.

b. The CRI solution is analyzed to check the accuracy of the instrument down near the contract required detection limits (CRDL). It is analyzed in conjunction with the interference check sample. The sample is prepared from a purchased solution which contains 120 µg/mL Sb, 100 µg/mL Co and V, 80 µg/mL Ni, 50 µg/mL Cu, 40 µg/mL Zn, 30 µg/mL Mn, 20 µg/mL As, Cr, Ag and Tl, 10 µg/mL Be, Cd and Se along with 6 µg/mL Pb. 500 µ/L of the solution is diluted to 500 mL. This solution is stable for 6 months.

b. The interference check solutions (ICSA and ICSAB) are prepared to contain known concentrations of interfering elements that will provide an adequate test of the IECs. A solution containing 500 ug/mL Al, Ca, Mg and 200 ug/mL Fe is diluted 10x to prepare the ICSA. The ICSAB is prepared by diluting 100x a solution containing 10 ug/mL of As and Tl; 20 ug/mL Ag; 50 ug/mL Ba, Be, Cr, Co, Cu, Mn, and V; 100 ug/mL Cd, Ni and Zn; 5 ug/mL Pb and Se; and 60 ug/L Sb. Add to this a solution containing 500 ug/mL Al, Ca, Mg and 200 ug/mL Fe diluted 10x. These solutions are prepared as needed or monthly.

d. Reporting Limit Standard- Prepared 1.0 ml of RL Stock solution A and 1.0 ml of RL Stock Solution B diluted to 100 ml with 2% HNO3 and 5% HCL matrix , mix well. Solution stable for 3 months

6. Digestion standards

a. The Laboratory control sample (LCS) is prepared from High Purity solutions CLP-CAL-1 solution A and B; CLP-CAL-2 and CLP-CAL-3. 0.50 mL of CLP-CAL-1 A and B is diluted to 500 mL with 0.125 mL of CLP-CAL-2 and CLP-CAL-3. 25 mL of HCl and 10 mL of HNO3 are added for preservation. This solution is stored in a Teflon bottle. A portion is reserved in case of a problem with digestion. When there is a problem with the analysis of the LCS the solution is checked first before action is taken to make sure that it was made properly and has not deteriorated since it was made up. This solution is given a unique identifier. The LCS is prepared from a source independent from that used in the calibration standards. This solution is prepared daily or as needed. Note: The analysis of Molybdenum is not a routine procedure but a project-specific requirement. A customized LCSW mix must be prepared to contain this target analyte.

b. The solid Laboratory Control Sample (Soil) (LCSS) is prepared by weighing up 1.0 g of teflon chips and spiking using the same spiking solutions used to spike the sample matrix. This standard is given a unique identifier i.e. LCSS(date prepared)A,B,C etc.

c. The spiking solutions are prepared as follows:

1. Stock Multi-element Spiking Solutions: High Purity CLP-CAL-1 solution A: 2000 ug/mL Al and Ba; 50 ug/mL Be; 200 ug/mL Cr; 500 ug/mL Co, Mn, Ni, V and Zn; 250 ug/mL Cu; 1000 ug/mL Fe; 5000 ug/mL Ca, Mg, K and Na; solution B: 250 ug/mL Ag; CLP-CAL-2: 1000 ug/L Sb; CLP-CAL-3: 1000 ug/mL As, Pb, Se, Tl; 500 ug/mL Cd. Order from the manufacturer already prepared. These solutions are given a unique identifier. Add 0.050 mL (0.20 mL for soil samples) of CLP-CAL-1 solutions A and B, and 0.0125 mL (0.05 mL for soil samples) of CLP-CAL-2 and 3 to 50 mL of sample (1gram of sample for soils) for the following spike values: 2000 ug/L Al and Ba; 50 ug/L Be; 200 ug/L Cr; 500 ug/L Co, Mn, Ni, V and Zn; 250 ug/L Cu; 1000 ug/L Fe; 5.0 mg/L Ca, Mg, K and Na, 250 ug/L Ag, Sb, As, Pb, Se and Tl; 125 ug/L Cd. A blank spike should be prepared at the time the samples are spiked to check the actual spike value and accuracy.

2. TCLP Spiking Solution: Use 0.50 mL diluted to 50 mL for digestion:
2.5 mL 10000 mg/L Ba stock standard diluted to 100 mL; 2.5 mL Cr, Pb and As 1000 mg/L stock standard diluted to 100 mL; 0.50 mL Cd and Se diluted to 100 mL . Store in a Teflon bottle. A blank spike should always be prepared at the same time a sample is being spiked. This solution should produce a spike value of 2500 ug/L Ba; 250 ug/L Cr, Pb and As; and 50 ug/L of Cd and Se. Note: Since the samples are diluted 10x when digested the spike value will appear to be 10x greater when analyzed.

3. TCLP Silver Spiking Solution: Use 5.0 mL diluted to 50 mL for digestion:
0.40 mL of 1000 mg/L stock Ag solution diluted to 100 mL. Store in a Teflon bottle. A blank spike should always be prepared at the same time a sample is being spiked. This solution should produce a spike value of 400 ug/L. . Note: Since the samples are diluted 10x when digested the spike value will appear to be 10x greater when analyzed. Also this solution is not very stable and may require fresh preparation at least weekly.

VIII. CALIBRATION AND ASSOCIATED QA/QC

A. Set up the instrument with proper operating parameters. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

B. Operating conditions - **The instrument settings can be found in method file.** For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

C. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions. **(See SOP-106, *ICP Instrument Operation*)** Flush the system with 2% HNO_3 / 5% HCl between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve consists of a blank and three standards ($r \geq 0.995$). If a three point

calibration curve is not required for the client samples being analyzed Empirical Laboratories may use a blank and one standard as referenced in USEPA - CLP protocols.

D. Before beginning the sample run, analyze the Iron and Aluminum standards at their linear range to check for IEC drifts. Analyze these standards first as QC samples with an IEC check table and action taken should be to calculate IECs. Then reanalyze the standard as a sample to check to see if the correction was made successfully. If the IEC correction overcompensated or under compensated for any one metal which is affected by it, the standard should be run again as a QC as before. Make sure to rinse thoroughly after running these linear range standards, they can cause carry over into the initial QC samples which are analyzed next. The analysis order follows as: ICV (± 10%) for 200.7 (± 5%) and ICB (< ±MDL or ±RL/CRDL for others or CLP, **for CCB, DOD QSM Ver. 3 no analytes detected >2xMDL**) first, then reanalyze the highest mixed calibration standard(s) as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5%. If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

E. For CLP projects,verify the validity of the curve in the region of 2x the contract required detection limit (CRDL) before and after each batch of 20 samples in the specific order of CRI, ICSA, ICSAB, CCV and CCB(CCB criteria: < ±MDL or ±RL/CRDL for others or CLP, **for CCB, DOD QSM Ver. 3 no analytes detected >2xMDL, beginning and end of sequence and after every 10 samples**) or twice during every 8-hour work shift, whichever is more frequent. Results should be within ±20%. Supervisor must be notified if the control limit is not met. Supervisor will dictate corrective action if required. The final analytical report must document this situation. (For Internal QC)

F. Verify the interelement and background correction factors at the beginning and after each batch of 20 samples in the specific order of CRI, ICSA, ICSAB, CCV and CCB(CCB criteria: < ±MDL or ±RL/CRDL for others or CLP, **for CCB, DOD QSM Ver. 3 no analytes detected >2xMDL, beginning and end of sequence and after every 10 samples**) or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check solution A and AB. Results should be within ±20% of the true value for ICSAB. **For ICSA DOD QSM Ver 3. , absolute value of concentration for all non-spiked analytes < 2xMDL**.(ICSAB required at the end for CLP projects)

G. *When analyzing samples associated with North Carolina or with DOD QSM Ver. 3 work, a solution containing analytes at their reporting limit must be analyzed prior to sample analysis. The concentrations must be within 20% DOD(20 or 30% depending on project) of their true values to be acceptable.*

Note: Supervisor must be notified if the control limit is not met. Supervisor will dictate corrective action if required. The final analytical report must document this situation.

H. The instrument must be calibrated once every 24 hours if performing straight CLP work.

I. **Note: The instrument software is set up to go to the "L" rack for calibration standards, initial IEC standards and initial and continuing calibration verifications (ICV/CCV). This QC is inserted by the analyst when setting up the autosampler table which is what the instrument software uses for a RUN LOG (The software does not allow the analyst to print the actual run log but prints an autosampler report). The autosampler report is used to load the instrument and does not include ICV and CCVs in racks 2 through 5 because all calibration QC is loaded in the "L" rack and then samples and CCB's are loaded in Racks 2 through 5. When the samples are analyzed the software inserts ICVs and CCVs from the actual run log set up by the analyst. Since each CCV location is visited twice by the autosampler during the run, two locations will be called CCV1 and two locations will be CCV2 and so on. The time and date are printed on the instrument print out with the data so that the data user can distinguish between the two CCVs.**

J. Instrument Autosampler Report example:

Calibration or "L" Rack(used by instrument software to insert QC)

1) STD 1-blank
2) NAK-100ppm
3) NAK-high
4) Fe-500,000ppb
5) Mn-10,000ppb
6) QC 21-high
7) Al IEC-QC(calculate IEC)
8) FE IEC-QC(calculate IEC)
9) ICV
10) CCV1
11) CCV2
12) CCV3

Sample Sequence RACK 1

1) Al IEC-(readback)
2) Fe IEC-(readback)
3) ICB-initial
4) RL-reporting limit standard
5) NAK 100ppm-(readback)

Sample Sequence RACK 1 (cont.')

6) NAK High-(readback)
7) QC 21 High-(readback)
8) Rinse
9) CRI-0
10) ICAS-0
11) ICASB-0
12) Rinse
13) CCB 1A
14) Preparation Blank
15) Laboratory Control Sample
16) Sample 1
17) Sample 2
18) Sample 3
19) Sample 4
20) Sample 5
21) Sample 6
22) Sample 7
23) Sample 8
24) CCB 1B
25) Sample 9
26) Sample 10
27) Sample 11
28) Sample 12
29) Sample 13
30) Sample 14
31) Sample 15
32) Sample 16
33) Sample 17
34) Sample 18
35) CCB2A
36) Sample 19
37) Sample 20
38) Sample serial dilution
39) Sample matrix spike
40) Sample matrix spike duplicate
41) Sample post digestion spike
42) CRI-1
43) ICSA-1
44) ICSAB-1
45) Rinse
46) CCB 2B
47) Preparation Blank
48) Laboratory Control Sample

RACK 2

1) Sample 1
2) Sample 2
Etcetera...

Each rack holds 48 samples and there are 4 racks that are used for samples and CCBs and run QC other then ICV/CCV's.

IX. PROCEDURE

A. Once the instrument has been calibrated, begin the analysis of samples.

B. If particulates are visible in the digestate, the sample must be filtered prior to analysis. If filtration is required, a filter blank must be prepared by filtering reagent grade water which has been properly acidified. **In the event USACE samples are filtered, all USACE samples and the QC samples in that QC batch must be filtered. All USACE solid samples and their associated batch QC samples must be filtered prior to analysis.**

C. Flush the system with 2% HNO_3 / 5% HCl for at least 1 minute before the analysis of each sample.

D. Dilute and reanalyze samples that are more concentrated than the linear calibration limit or, for 200.7, $\pm$ 10% of the linear range standard. **In the case of USACE samples, the criterion changes and requires dilution and reanalysis of all samples which produce a concentration that exceeds the highest calibration standard. Sample results detected between the MDL and RL are flagged as estimated with a "B" flag.**

E. Verify calibration every 10 samples or every 2 hours, whichever is more frequent and at the end of the analytical run, using a continuing calibration verification (CCV) sample and a continuing calibration blank (CCB) sample.

- The results of the CCV are to agree within 10% for 6010 (5% for 200.7) on initial verification of the expected value, with relative standard deviation (RSD) < 5% from replicate (minimum of two integrations). If not, terminate the analysis, correct the problem, and reanalyze the previous ten samples. The analyst may continue the analytical run, and after conferring with the section manager it may be necessary to reanalyze a group of samples. The analyst must notify the section manager within 24 hours.

- The results of the calibration blank (this is not the method/preparation blank) are to agree within < ±MDL(SW-846 Method 6010B), and 3 x IDL or CRDL for CLP, for **DOD QSM Ver. 3 no analytes detected >2xMDL**. If the calibration blank is not in control, evaluate the impact

upon the previous 10 samples. Reanalysis may be required after an evaluation of the data. If the blank < 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, samples need not be reanalyzed. One must also evaluate the reporting limit (RL) as it relates to 3X the IDL/MDL. If the RL is significantly above 3X IDL or MDL then reanalysis may not be required (Na, K, Mg and Ca are good examples of this situation).

- Total hardness is reported from HNO_3 preserved sample. The final concentration is calculated from the calcium and magnesium results as follows:

  Ca mg/L x 2.5 + Mg mg/L x 4.1 = total Hardness in mg/L as $CaCO_3$

F. Documentation of Capability (DOC) – Each analyst must perform a DOC to demonstrate proficiency with this method. Refer to SOP-413 for guidance.

X. CALCULATIONS

A. The instrument will generate data results in mg/L or µg/L (labeled appropriately). Each result represents an average of three individual readings per metal channel.

B. For aqueous samples, if a post/predigestion dilution is performed , the result must be multiplied by this factor or the dilution factor must be entered into the instrument data table in which case the instrument will generate data corrected for the dilution.

C. For solid samples, if a postdigestion dilution is performed , the result must be multiplied by this factor or the dilution factor must be entered into the instrument data table in which case the instrument will generate data corrected for the dilution. Also, the result must be converted to reporting units which are usually mg/kg.

SR (ug/g or mg/kg) = IR*DF*FED/SM

SR	=	Sample result
IR	=	Instrument result (µg/L)
DF	=	Dilution factor (post digestion)
FED	=	Final volume of digestate (L)
SM	=	Sample mass digested(g)

XI. QUALITY CONTROL

A. Daily

1. See sections VIII and IX above.

B. Quarterly

1. Linear range standards must be analyzed at a frequency no less than once every three months. The linear range standard represents the second standard required for verification that samples are actually linear to the degree claimed. The analyst is responsible for completing this task in a timely manner. The linear range standard must be within +/-5% of true value.

2. The interelement correction factors (IEC) should be verified at the time the linear range standards are analyzed.

3. IDL's if CLP work required.

C. Digestion

1. All quality control data should be maintained and available for easy reference or inspection.

2. Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank, sometimes referred to as the preparation blank is a volume of reagent water acidified with the same amounts of acids as were the standards and samples. These blanks are taken through the same digestion/preparation steps as the sample being tested. The result for the method blank should not indicate contamination greater than ± ½ RL (USACE) or ±RL/CRDL for other or CLP. If exceeded, the impact upon the data should be evaluated and the associated sample(s) should be either redigested or the data should be qualified.

3. Employ a minimum of one laboratory control sample (LCS) for aqueous samples or one teflon chip spiked sample per sample batch to verify the digestion procedure. These LCSs are taken through the same digestion/preparation steps as the sample being tested. The control limits are ±15% method 200.7 - aqueous and soil samples or ±20% for all other methods aqueous and soil samples. If the LCS is not in control, the impact upon the client data should be evaluated and the associated sample(s) should be redigested. Consult your supervisor for further action. Qualifying the associated data may not be permissable for CLH.

D. Sample

1. Analyze one replicate sample for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. It is acceptable to substitute a matrix spike duplicate for the sample replicate. Project specific requirements will take precedence in these

situations. NJDEP demands that this requirement be met with a client specific duplicate rather than a spike duplicate. The control limits are 20% RPD (if both are >5x CRDL) or ± the CRDL (if either are <5X CRDL).

2. Analyze one spiked sample and spiked sample duplicate for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. Project specific requirements will take precedence in these situations. If the analyte level in the sample is not greater than 4X the spiking level, the spike recoveries should be within ±25% of the true value. If not, a post digestion spike should be analyzed.

    i. CLH requires an additional high-level matrix spike for chromium. The spike must be analyzed on a client-designated sample and be performed in addition to the low-level spike at a frequency of one per batch. The high-level spike concentration shoud be 10 times the low-level spike (ex. 40 mg/kg for chromium low-level spike and 400 mg/kg for the high-level spike.) Note that the high-level spike requirement is for chromium only. Recovery requirements are 75% to 125% for both the low-level and the high-level matrix spike.

3. The relative percent difference (RPD) between replicate determinations is to be calculated as referenced in the laboratory QA manual. (A control limit of ± 20% RPD (non-aqueous samples may routinely exceed this amount) shall be used for sample values greater than five times the contract required detection limit.) Supervisor must be notified if the control limit is not met. Supervisor will dictate corrective action if required. The final analytical report must document this situation.

4. *The following should be analyzed with each preparation batch containing a matrix spike.*

    - Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 50 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution (volumetric glassware must be used) should agree within ±10% of the original determination. If not, a chemical or physical interference effect should be suspected. The analyst and or section manager must note this situation on the final analytical report.

    - Post digestion spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 85% to 115% of the known value and is required if the pre-digestion matrix spike (low-level only for CLH) is outside of control limits. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be

suspected. The analyst and or section manager must note this situation on the final analytical report.

E. Method Detection Limit (MDL), Empirical Laboratories Reporting Limit (ERL), Contract Required Quantitation Limit (CRQL) and Analyte Wavelength:

TABLE I

Aqueous and Soil Method Detection Limits(MDL), Empirical Laboratories Reporting Limits(ERL), CLP OLM04.1 & OLM05.2 Contract Required Quantitation Limits (CRQL)

Analytes by EPA 200.7,3005A/3050A- 6010B SOW 4.1 & 5.2	AQUEOUS MDL (ug/L)	AQUEOUS ERL (ug/L)	AQUEOUS CRQL ILMO 4.1 (ug/L)	AQUEOUS CRQL ILMO 5.2 (ug/L)	SOLID/SOIL MDL (mg/Kg)	SOLID/SOIL ERL (mg/Kg)	SOLID/SOIL CRQL ILMO 4.1 (mg/Kg)	SOLID/SOIL CRQL ILMO 5.2 (mg/Kg
Silver	**1.0**	**10**	**10**	**10**	**0.20**	**2.0**	**2**	**2**
Aluminum	**50**	**200**	**200**	**200**	**10**	**40**	**40**	**40**
Arsenic	**3.0**	**10**	**10**	**15**	**0.6**	**2.0**	**2**	**3**
Barium	**5.0**	**200**	**200**	**200**	**1.0**	**40**	**40**	**40**
Beryllium	**1.0**	**5.0**	**5**	**5**	**0.20**	**1.0**	**1**	**1**
Calcium	**200**	**5000**	**5000**	**5000**	**20**	**1000**	**1000**	**1000**
Cadmium	**1.0**	**5.0**	**5**	**5**	**0.20**	**1.0**	**1**	**1**
Cobalt	**5.0**	**50**	**50**	**50**	**1.0**	**10**	**10**	**10**
Chromium	**2.0**	**10**	**10**	**10**	**0.40**	**2.0**	**2**	**2**
Copper	**4.0**	**25**	**25**	**25**	**0.40**	**5.0**	**5**	**5**
Iron	**30**	**100**	**100**	**100**	**1.0**	**20**	**20**	**20**
Potassium	**200**	**5000**	**5000**	**5000**	**40**	**1000**	**1000**	**1000**
Magnesium	**200**	**5000**	**5000**	**5000**	**40**	**1000**	**1000**	**1000**
Manganese	**1.0**	**15**	**15**	**15**	**0.20**	**3.0**	**3**	**3**
Sodium	**200**	**5000**	**5000**	**5000**	**40**	**1000**	**1000**	**1000**
Nickel	**3.0**	**40**	**40**	**40**	**1.0**	**8.0**	**8**	**8**
Lead	**1.5**	**3.0**	**3**	**10**	**0.60**	**0.60**	**0.6**	**2**
Selenium	**3.0**	**5.0**	**5**	**35**	**0.60**	**1.0**	**1**	**7**
Antimony	**5.0**	**60**	**60**	**60**	**1.0**	**12**	**12**	**12**
Thallium	**3.0**	**10**	**10**	**25**	**0.60**	**2.0**	**2**	**5**
Vanadium	**5.0**	**50**	**50**	**50**	**1.0**	**10**	**10**	**10**
Zinc	**5.0**	**20**	**20**	**60**	**1.0**	**4.0**	**4**	**12**

TABLE 2

METAL	WAVELENGTH
Aluminum	308.2
Antimony	206.8
Arsenic	189.0
Barium	493.4
Beryllium	313.0
Cadmium	226.5
Calcium	317.9
Chromium	267.7
Cobalt	228.6
Copper	324.7
Iron	271.4
Lead	220.3
Magnesium	279.0
Manganese	257.6
Nickel	231.6
Potassium	766.4
Selenium	196.0
Silver	328.0
Sodium	330.2
Thallium	190.8
Vanadium	292.4
Zinc	206.2

XII. CORRECTIVE ACTIONS

A. INSTRUMENT RELATED

1. ICV not within ± 10% or ± 5% for 200.7
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.

b. Is the problem with the calibration?
   i. Recalibrate through analysis of appropriate standards and recheck ICV.

2. ICB not ±MDL or within ± 3X IDL or CRDL for CLP, **DOD QSM Ver. 3 no analytes detected >2xMDL**

   a. Is the problem with the solution?
      i. Reprepare
   b. Is the problem with the calibration?
      i. Recalibrate with the blank solution or the low level standard. Restart analysis with the ICV.

3. Check standards not within ± 5%
   a. Is the problem with the solution?
      i. Repour, reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.

4. CRI not within ± 20% (Internal QC, only required for CLP work).
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.
5. ICSA metals not present are not less than the CRDL for that metal, **for ICSA DOD QSM Ver 3. , absolute value of concentration for all non-spiked analytes < 2xMDL.**
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.

6. ICSAB not within ± 20%
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?
      i. Recalibrate thru analysis of appropriate standards. Restart analysis with the ICV.

7. CCV not within ± 10%
   a. Is the problem with the solution?
      i. Reprepare or obtain new stock.
   b. Is the problem with the calibration?

i. If appropriate, continue the analysis. Discuss effect of the out of control situation with your supervisor. The samples will be reanalyzed or the data will be qualified. Note: CLH data must always be reanalyzed back to the last compliant CCV and not qualified.

8. CCB not ±MDL or within ± 3X IDL or CRDL for CLP, **DOD QSM Ver. 3 no analytes detected >2xMDL**
   a. Is the problem with the solution?
      i. Reprepare
   b. Is the problem with the calibration?
      i. Apply SW846 guidance. (See Section IX-E for additional guidance). Note: CLH data must always be reanalyzed back to the last compliant CCB and not qualified.

B. DIGESTION RELATED

1. Preparation blank not within ± ½ RL and ± RL for common contaminants USACE or RL/CRDL for other or CLP
   a. Is the problem with the instrument?
      i. Evaluate with respect to instrumental bias or reanalyze when instrument is in control.
   b. Is the problem with the digestion?
      i. If associated samples are less than 10X the level of the preparation blank but above the RL, the sample must be redigested or the data must be qualified on the final report.

2. LCS not within control limits
   a. Is the problem with the instrument?
      i. Evaluate with respect to instrumental bias or reanalyze when instrument is in control.
   b. Is the problem with the digestion?
      i. If biased low, associated samples must be redigested.
      ii. If biased high, the impact upon the data user must be evaluated. The samples will be redigested or the data will be qualified on the final report.

C. SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20% (if both are >5X CRDL) or ± the CRDL (if either are <5X CRDL).
   a. The associated sample data must be qualified on the final report.

2. Spike analysis recovery not within ±20%

a. Is the analyte level in the sample greater than 4X the spiking level?
   i. If yes, the spike recovery is not evaluated.
   ii. If no, a post digestion spike must be analyzed and the associated sample data must be qualified on the final report.

b. The spike requirements for CLH are as follows: Both a high level and a low level spike performed on a CLH disignated sample at a frequency of one per batch. The high level spike at 10X greater than the low level spike. (ie. 40 mg/kg for chromium low-level spike and 400 mg/Kg for the high-level spike.) Note that the high-level spike is for chromium only. Recovery requirements are 75 to 125% for both the low-level and the high-level matrix spike.

3. When required, post digestion spike analysis recovery not within ±15%.
   a. The associated sample data must be qualified on the final report.
   b. For USACE analysis by MSA is required.

4. Serial dilution analysis percent difference not within ±10%
   a. Is the analyte concentration a factor of 50 above the instrumental detection limit after dilution?
      i. If no, the serial dilution data can not be evaluated.
      iii. If yes, a chemical or physical interference effect should be suspected. The analyst and or section manager must note this situation on the final analytical report.

XIII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405 fot instruction of proper disposal of waste generated from this area.

Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIV. REFERENCES

1. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846; Third Edition (Update III)*; Method 6010B

2. USEPA *Code of Federal Requlations, 40, CH 1,PT 136;* Method 200.7; APX-B

3. USEPA *Contract Laboratory Program(CLP) for Inorganics ILM04.1; ILM05.2*

Refer to SOP-431 for common environmental laboratory definitions.

Addendum for USEPA CLPILM 05.2

1. The control limit for the ICSA is at 20% or ±CRQL whichever is greater.
2. Preparation codes are required in the digestion log See SOW Exhibit B for a listing of these codes with definitions.
3. The CRQL check standard is run at the concentration of the respective CRQLs. For a listing of CRQL for this SOW see Exhibit C. Several of the metals concentration levels have changed.
4. The spiking level for CLP ILM 05.2 is at 50 ug/L for selenium. All other spike levels remain the same as in SOW ILM 04.1.
5. The CCV shall be analyzed at a different concentration then the ICV (at or near one-half of the calibration standard concentration.
6. The post digestion spike must be analyzed at 2x the indigenous level of the sample or two times the CRQL whichever is greater.
7. A Non-prepared MDL study must be analyzed and the results of this study used for MDL reporting when sample volumes are not digested.

CHANGES TO FORMS for SOWCLPILM 05.2

1. Forms must be double-sided
2. A photocopy of the instrument's direct sequential readout shall be included.
3. Undiluted samples must be reported as well as diluted samples.
4. J flags are used in place of B flags when a sample has a concentration less the CRQL but greater then or equal to the MDL.
5. A D flag is used for samples reported from a dilution.
6. All results are reported down to the MDL not the IDL.
7. Preparation codes are used on form 13.

The form for method of standard additions (MSA) has been removed and all subsequent QC has move up one form number in other words form 8 is now serial dilution when it used to be the MSA form,etcetera.

ANALYST DATA REVIEW CHECKLIST Sample Number(s):
Batch Number(s):
Method: 6010B (ICP)

QA/QC Item	Yes	No	NA	Second Level Review
1. Were samples analyzed within USACE holding times?				
2. Was initial calibration curve QC criteria met?				
3. Was all continuing calibration criteria in control?				
4. Did any sample exceed the highest calibration standard? (If yes, were appropriate dilutions made to generate samples concentration within calibration range?)				
5. Did LCS or blank spike meet control limits?				
6. Did MS/MSD meet control limits?				
7. Was the preparation (Method) Blank below the project required detection limits?				
8. Did you return samples back to cold storage immediately after use?				
9. Was hot plate temperature monitored/documented and did you apply the thermometer correction factor?				
10. Sample preparation information is correct and complete.				
11. Analytical results are correct and complete.				
12. The appropriate SOP's have been used and followed.				
14. "Raw data" including all manual integration's have been correctly interpreted.				
15. "Special" sample preparation and analytical requirements have been met.				
16. Documentation complete (e.g., all anomalies in the analytical sequence have been documented, corrective action forms are complete.				

Comments on any "No" response:

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

INORGANIC RAW DATA AND REPORT CHECK

SOP NUMBER: SOP-118

REVISION NUMBER: 1

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 12/05/03

DATE OF LAST REVIEW: 01/17/06

INORGANIC RAW DATA AND REPORT CHECK

I. SUMMARY

The following describes the process through which the raw data is initially checked after analysis.

A. Data Format

There is a check sheet which is specific to each chemistry located in *V:/lab/wetchem/tests/***"specific chemistry"** *data 2nd check.doc*. Obtain the appropriate check form for the specific chemistry being performed.

B. Primary Analyst Check

The primary analyst is responsible for checking that samples meet all the appropriate method criteria and that all information is documented on the raw data sheet. (If criteria are not met, a CAR is generated within 24 hours and forwarded to the inorganic manager.) The check sheet is filled out by the analyst affirming that all QC meets criteria and that information is complete, the sheet is then turned in with the raw data to the report generator.

C. Report Generator Check

The report generator 2nd checks the data and affirms that the check sheet has been filled out appropriately and that all QC has been performed within specified limits or that a CAR has been attached to the data. Then data is entered into the LIMS system and the report is generated.

D. Inorganic Manager Check

The inorganic Manager checks the report to make sure it is in the format required by the client. A case narrative is generated if requested by the client and the report is evaluated for conflicting or unusual results. Items, which seem questionable are checked against the data and/or discussed with the analyst. The report is then forwarded to the Project Manager, PM, who generates and invoice and forwards everything to the division director to be evaluated, signed and mailed out.

DETERMINATION OF INORGANIC ANIONS IN WATER BY ION CHROMATOGRAPHY USING THE DIONEX DX-500 ION CHROMATOGRAPH WITH HYDROXIDE ELUENT AND DIONEX COLUMN AS18 BY METHOD 300.0 GUIDANCE

SOP NUMBER: SOP-145

REVISION NUMBER: 4

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: 11/28/06

DATE OF LAST REVIEW: 11/28/06

DETERMINATION OF INORGANIC ANIONS IN WATER BY ION CHROMATOGRAPH USING THE DIONEX dx-500 ION CHROMATOGRAPH WITH HYDROXIDE ELUENT AND DIONEX AS18 COLUMN

References:
USEPA METHOD 300.0

I. SCOPE AND APPLICATION:

1. This method covers the determination of the following inorganic common anions in reagent water, surface water, ground water, and other aqueous matrixes.

PART A.--Common Anions

Chloride	Nitrate	Fluoride	Sulfate
Nitrite	Bromide	Ortho Phosphate	

2. Single laboratory Method Detection Limit for the above analytes is listed in Tables 1A, 1B and 1C from method 300.0. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample and the specific instrumentation employed.

   A. In order to achieve comparable detection limits, an ion chromatographic system must utilize suppressed conductivity detection, be properly maintained and must be capable of yielding a baseline with no more then a 5 nS noise/drift per minute of monitored response over the background conductivity.

3. This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

4. When the method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a laboratory fortified matrix sample covering the anions of interest. The fortification procedure is described in the Quality Control section.

5. Users of the method data should state the data-quality objectives prior to analysis. Analyst using this method must demonstrate the ability to generate acceptable results with the method, using the procedures described in the Quality Control section.

II. SUMMARY OF METHOD

1. A small volume of sample, 50 uL for Part A is introduced into an ion chromatograph (IC). The anions of interest are separated and measured, using a

system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

III. DEFINITIONS

1. **ANALYSIS BATCH** -- A group of no more than 20 field samples (Field sample analyses include only those samples derived from a field sample matrix. These include the initial and duplicate field samples as well as all Laboratory Fortified Sample Matrices). The analysis batch must include an Initial Calibration Check Standard, and End Calibration Check Standard, Laboratory Reagent Blank, and a Laboratory Fortified Blank. Within an ANALYSIS BATCH, for every group of **ten** field samples at least one Laboratory Fortified Matrix (LFM) and either a Field Duplicate, a Laboratory Duplicate or a duplicate of the LFM must be analyzed after the tenth field sample analysis.

2. **CALIBRATION STANDARD (CAL)** -- A solution prepared from the primary dilution standard solution or stock standard solutions and the surrogate analyte. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

   A. **INITIAL CALIBRATION STANDARDS --** A series of CAL solutions used to initially establish instrument calibration and develop calibration curves for individual target anions.

   B. **INITIAL CALIBRATION CHECK STANDARD** -- An individual CAL solution, analyzed initially, prior to any sample analysis, which verifies previously established calibration curves.

   C. **CONTINUING CALIBRATION CHECK STANDARD** -- An individual CAL solution which is analyzed after every tenth field sample analyses which verifies the previously established calibration curves and confirms accurate analyte quantitation for the previous ten field samples analyzed.

   D. **END CALIBRATION CHECK STANDARD** -- An individual CAL solution which is analyzed after the last field sample analyses which verifies the previously established calibration curves and confirms accurate analyte quantitation for all field samples analyzed since the last continuing calibration check.

3. **FIELD DUPLICATES (FD) --**Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout the field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

4. **INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) --** A solution of one or more method analytes, surrogates or other test substances used to

evaluate the performance of the instrument system with respect to a defined set of criteria.

5. **LABORATORY DUPLICATE** -- Two sample aliquots, taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated specifically with the laboratory procedures, removing any associated variables attributed by sample collection, preservation, or storage procedures.

6. **LABORATORY FORTIFIED BLANK (LFB)** --An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

7. **LABORATORY FORTIFIED SAMPLE MATRIX (LFM)** -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

8. **LABORATORY REAGENT BLANK (LRB)** -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

9. **LINEAR CALIBRATION RANGE (LCR)** -- The concentration range over which the instrument response is linear.

10. **MATERIAL SAFETY DATA SHEET (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

11. **METHOD DETECTION LIMIT (MDL)** -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

12. **MINIMUM REPORTING LEVEL (MRL)** -- The minimum concentration that can be reported for an anion in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

13. **PERFORMANCE EVALUATION SAMPLE (PE) --** A certified solution of method analytes whose concentration is unknown to the analyst. Often, an aliquot of this solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst.

14. **QUALITY CONTROL SAMPLE (QCS) --** A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

15. **STOCK STANDARD SOLUTION (SSS) --** A concentrated solution containing one or more method analytes prepared in the laobratory using assayed reference materials or purchased from a reputable commercial source.

IV. INTERFERENCES

1. Interferences can be divided into three different categories: **direct chromatographic coelution**, where an analyte response is observed at very nearly the same retention time as the target anion; **concentration dependant coelution**, which is observed when the response of higher than typical concentrations of the neighboring peak overlap into the retention window of the target anion; and, **ionic character displacement**, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analytes's retention times.

   A. A direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect. The analyst must verify that these changes do not negatively affect performance by repeating and passing all the criteria in the Quality Control Section.

   B. Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant coelution or ionic character displacement, but it must be clarified that sample dilution will alter your Minimum Reporting Limit (MRL) by a proportion equivalent to that of the dilution. Therefore, careful consideration of project objectives should be given prior to performing such a dilution. An alternative to sample dilution, may be dilution of the eluent.

C. Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. Prior to using any pretreatment, the analyst should be aware that all **instrument calibration standards must be pretreated in exactly the same manner** as the pretreated unknown field samples. The need for these cartridges has been greatly reduced with recent advances in high capacity anion exchange columns.

1. Extreme caution should be exercised in using these pretreatment cartridges. Artifacts are known to leach from certain cartridges, which can foul the guard, and analytical columns causing loss of column capacity indicated by shortened retention times and irreproducible results. Frequently compare your calibration standard chromatograms to those of the column test chromatogram (received when the column was purchased) to insure proper separation and similar response rations between the target analytes is observed.

D. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in an ion chromatogram. These interferences can lead to false positive results for target analytes as well as reduced detection limits as a consequence of elevated baseline noise.

E. Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

F. Any anion that is only weakly retained by the column may elute in the retention time window of fluoride and potentially interfere. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant; however, it is the responsibility of the analyst to generate precision and accuracy information in each sample matrix.

G. Close attention should be given to the potential for carry over peaks from one analysis which will effect the proper detection of analytes of interest in a second, subsequent analysis. The elution of nitrate (retention time of ~9.0 min.) indicates the end of a chromatographic run. A run time of 12 minutes is recommended to allow for the proper elution of any potentially interferrant late peaks. It is the responsibility of the analyst to confirm that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

2. SAFETY

A. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential heath hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

B. Your laboratory manager and/or Safety Officer is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. A formal safety plan is also available. Use proper personal protection equipment, PPE, such as safety glasses, gloves and laboratory coats should be warn when handling samples and chemicals.

V. EQUIPMENT AND SUPPLIES

1. Ion Chromatograph (IC) – Analytical system complete with eluent generator, an ion chromatographic pump, injection valves, both guard and analytical separator columns, suppressor, conductivity detector, and computer based data acquisition system. Dionex DX-500 or equivalent. (See letter from EPA to Dionex on discussion of alternate hydroxide eluent for anions. Also since hydroxide eluent cannot be run on the traditional column Dionex AS18, 4mm (P/N 060549) or equivalent should be used.

   a. Anion guard column--Dionex Ion Pac AG18 4mm (P/N 060551), or equivalent. This column functions as a protector of the separator column. If omitted from the system, the retention times will be shorter.

   b. Anion separator column--Dionex Ion Pac AS18, 4mm (P/N 060549), or equivalent. An optional column (2mm or 4 mm) may be used if comparable resolution of peaks is obtained, and the quality control requirements can be met.

      i. When a 4 mm column is employed, the injection volume should be 50 uL.

      ii. Comparable results can be attained using the Dionex, AS17, 4 mm column.

2. Anion suppressor device--The data presented in this method were generated using an Ultra 4 mm Dionex Anion Self Regenerating Suppressor (ASRS, P/N 53946). An equivalent suppressor device may be utilized provided comparable conductivity detection limits are achieved and adequate baseline stability is attained as measured by a combined baseline drift/noise of no more than 5 nS per minute over the background conductivity. Proper suppressor performance is essential to analytical data reproducibility and sensitivity of the conductivity detector.

   a. The ASRS was set to perform electrolytic suppression at a current setting of 300 ma using the external water mode. External water was delivered to the suppressor directly from a pressurized source at a flow rate of 5 mL/min. It should be noted that while Empirical Laboratories has the suppressor currently set at 300 mA, no external water is being used at this time.

3. Detector--Conductivity cell (Dionex CD20, or equivalent) capable of providing data as required in the Quality Control section of this SOP.

4. Data Acquisition System--The Dionex Peaknet Data Chromatography Software version 5.2 or equivalent is used by Empirical Laboratories.

5. Analytical balance--Mettler Used to accurately weigh target analyte salt for stock standard preparation (±0.1 mg sensitivity).

6. Micro beakers -- Plastic, disposable - used during sample preparation.

7. Syringes--Plastic, disposable, 10 mL - used during sample preparation.

8. Pipets -- Pasteur, plastic or glass, disposable, graduated, 5 mL and 10 mL.

9. Bottles -- High density polyethylene (HDPE) or glass, amber or clear, 30 mL, 125 mL, 250 mL. For sampling and storage of calibration solutions.

10. Particulate filters-- 0.45 micron syringe filters, specifically designed for IC applications (Gelman IC Acrodisc, PN 4485, or equivalent). These cartridges are used to remove particulates from the sample matrix while loading the sample manually or if the autosampler employed does not filter the sample during loading.

NOTE: See method for several types of pretreatment cartridges that are available and may be useful depending on the matrices of the samples normally processed.

11. Autosampler PolyVials 5-mL size, with filtercaps, 250 each --Dionex cat log # 38141.

12. Shaker for use when extracting soil samples.

13. Centrifuge to aid in separation after extraction.

14. Centrifuge tubes--50 mL capacity

VI. REAGENTS AND STANDARDS

1. Reagent water-- Distilled or deionized water 17.8 Mohm or better, free of anions of interest. Water should contain particles no larger than 0.20 microns.

2. A system or apparatus which automatically generates the hydroxide eluent (Dionex EG40, or equivalent) is an acceptable alternative to physically preparing the hydroxide eluent.

3. Stock standard solutions, 1000 mg/L (1mg/mL): Stock standard solutions are purchased as certified solutions from selected vendors.

   NOTE: Stability of standards: Stock standards for most anions are stable for at least 6 months when stored at 4 °C. Dilute working standards should be prepared monthly.

VII. SAMPLE COLLECTION, PRESERVATION AND STORAGE

1. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

2. Sample preservation and holding times for the anions that can be determined by this method are as follows:

PART A: Common Anions

Analyte	Preservation	Holding Time
Bromide	None required	28 days
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N	**Cool to 4 °C**	**48 hours**
Nitrite	**Cool to 4 °C**	**48 hours**
Ortho Phosphate	**Cool to 4 °C**	**48 hours**
Sulfate	Cool to 4 °C	28 days

3. When collecting a sample from a treatment plant employing chlorine dioxide, the sample must be sparged with an inert gas (helium, argon, nitrogen) prior to addition of the addition of the EDA preservative at time of sample collection.

VIII. QUALITY CONTROL

1. The laboratory is required to operate a formal quality control (QC) program. The requirements of this program consist of an initial demonstration of laboratory performance, and subsequent analysis in each analysis batch of a Laboratory Reagent Blank, Laboratory Fortified Blank, Instrument Performance Check Standard, calibration check standards, Laboratory Fortified Sample Matrices (LFM) and either Field, Laboratory or LFM duplicate sample analyses. This section details the specific requirements for each of these QC parameters. The laboratory is required to maintain performance records that define the quality of the data that are generated.

2. INITIAL DEMONSTRATION OF PERFORMANCE

   A. The initial demonstration of performance is used to characterize instrument performance (determination of accuracy through the analysis of the QCS) and laboratory performance (determination of MDLs) prior to performing analysis by this method.

   B. Quality Control Sample (QCS) – When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the

preparation and analyses of a QCS. If the determined concentrations are not within ±10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

C. Method Detection Limit (MDL)—MDLs are established for all analytes, using reagent water (blank) fortified at a concentration of three to five times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method over at least three separate days. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

Where,

t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].

S = standard deviation of the replicate analyses.

D. MDLs should be determined every 6 months or at least annually, when a new operator begins work or whenever there is a significant change in the background, or instrument response. MDL check samples are used in connection with confirming that the MDL determined is legitiment and to monitor the instrument sensitivity periodically. MDL checks are analyzed whenever a new MDL is generated and at a minimum quarterly to monitor for any shifts in sensitivity.

3. ASSESSING LABORATORY PERFORMANCE

A. Laboratory Reagent Blank (LRB) – The laboratory must analyze at least one LRB with each analysis batch. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL (**For DOD QSM Ver. 3 no analytes detected ≥ ½ RL or for common lab contaminants no analyte detected ≥ RL**) indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

B. Laboratory Fortified Blank (LFB)—The LFB should be prepared at concentrations similar to those expected in the field samples and ideally at the same concentration used to prepare the LFM. Calculate accuracy as percent recovery. If the recovery of any analyte falls outside the required concentration dependant control limits that analyte is judged out of control,

and the source of the problem should be identified and resolved before continuing analyses.

i. Control Limits for the LFB.

Concentration range	Percent Recovery Limits
MRL to 10x MRL	75 - 125%
10xMRL to highest calibration level	85 – 115%

ii. These control limits only apply if the MRL is established within a factor of 10 times the MDL. Otherwise, the limits are set at 90% to 110%.

iii. The laboratory uses the LFB to assess laboratory performance against the required control limits listed in the QC section. When sufficient internal performance data becomes available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x – 3S

The optional control limits must be equal to or better than those listed in the QC section (±10%). After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations monitored. These data must be on file and be available for review.

i. Instrument Performance Check Solution (IPC) – The Initial Calibration Check Standard is to be evaluated as the instrument performance check solution in order to confirm proper instrument performance. Small variations in retention time can be anticipated when a new solution of eluent (or when the KOH cartridge is changed) is prepared but if shifts of more that 2% are observed in the IPC retention time, some type of instrument problem is present. Potential problems improperly prepared eluent, erroneous method parameters programmed such as flow rate or some other system problem. The chromatographic profile (elution order) of the target anions following an ion chromatographic analysis should closely replicate the profile displayed in the test chromatogram that was shipped when the column was purchased. As a column ages, it is normal to see a gradual shift and shortening of retention times, but if after several years of use, extensive use over less than a year, or use

with harsh samples, this retention time has noticeably shifted to any less than 80% of the original recorded value, the column may require cleaning or replacement. Particularly if resolution problems are beginning to become common between previously resolved peaks. A laboratory must retain a historic record of retention times for all the target anions in the IPC to provide evidence of an analytical column's vitality.

4. ASSESSING ANALYTE RECOVERY AND DATA QUALITY

A. Laboratory Fortified Sample Matrix (LFM) – The laboratory adds a known amount of analyte to a minimum of 10% of the field samples within an analysis batch. The LFM sample is prepared from a sample matrix which has been analyzed prior to fortification. The analyte concentration must be high enough to be detected above the original sample and should adhere to the QC requirements. It is recommended that the solutions used to fortify the LFM be prepared from the same stocks used to prepare the calibration standards and not from external source stocks. This will remove the bias contributed by an externally prepared stock and focus on any potential bias introduced by the field sample matrix.

i. If the fortified concentration is less than the observed background concentration of the unfortified matrix, the recovery should not be calculated. This is due to the difficulty in calculating accurate recoveries of the fortified concentration when the native sample concentration is so high.

ii. The LFM should be prepared at concentrations no greater than five times the highest concentration observed in any field sample. If no analyte is observed in any field sample, the LFM must be fortified no greater than five times the lowest calibration level which as outlined in this method is the minimum reported level (MRL). For example, if chloride is not detected in any field samples above the lowest calibrations standard concentration of 5.00 ug/L, the highest LFM fortified concentration allowed is 25.0 ug/L.

iii. Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample. Percent recovery should be calculated using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where, R = percent recovery.
C_s = fortified sample concentration
C = sample background concentration

S = concentration equivalent of analyte added to sample.

iv. Until sufficient data becomes available (usually a minimum of 20 to 30 analysis), assess laboratory performance against recovery limits of 80 to 120%. When sufficient internal performance data becomes available develop control limits from percent mean recovery and the standard deviation of the mean recovery. The optional control limits must be equal to or better than the required control limits of 80 –120%.

v. If the recovery of any analyte falls outside the designated LFM recovery range and the performance for that analyte is shown to be in control, the recovery problem encountered with the LFM is judged to be matrix induced and the results for that sample and the LFM are reported with a "matrix induced bias" qualifier.

B. FIELD OR LABORATORY DUPLICATES –Analyze either a field or a laboratory duplicate for a minimum of 10% of the collected field samples or at least one with every analysis batch, whichever is greater. The sample matrix selected for this duplicate analysis must contain measurable concentrations of the target anions in order to establish the precision of the analysis set and insure the quality of the data. If none of the samples within an analysis batch have measurable concentrations, the LFM should be employed as a laboratory duplicate.

i. Calculate the relative percent difference (RPD) of the initial quantitated concentration (I_c) and duplicate quantitated concentration (D_c) using the following formula,

$$RPD = \frac{(I_c - D_c)}{([I_c + D_c]/2)} \times 100$$

ii. Duplicate analysis acceptance criteria

Concentration range	RPD Limits
MRL to 10xMRL	± 20%
10xMRL to highest calibration level	± 10%

iii. If the RPD fails to meet these criteria, the samples must be reported with a qualifier identifying the sample analysis result as yielding a poor duplicate analysis RPD. This should not be a chronic problem and if it frequently recurs (>20% of duplicate analyses) it indicates a problem with the instrument or individual technique.

C. Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

D. In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns, injection volumes, and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in the QC section and adhere to the condition of baseline stability.

E. The laboratory adopts additonal quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the client and the nature of the samples. Whenever possible, the laboratory performs analysis of quality control check samples and participate in relevant performance evaluation sample studies.

5. CALIBRATION AND STANDARDIZATION

A. Establish ion chromatographic operating parameters equivalent to those indicated in Tables 1C for a 4-mm column.

   i. Estimate the Linear Calibration Range (LCR) – The LCR should cover the expected concentration range of the field samples.

   ii. For an individual calibration curve, a minimum of eight calibration standards is required for a curve.

B. Prepare the calibration standards by carefully adding measured volumes of one or more stock standards to a volumetric flask and diluting to volume with reagent water. Chloride and sulfate are calibrated from 0.5-200 mg/L; fluoride, nitrate, and nitrite from 0.05-20 mg/L.

C. Using a 4mm column, inject 50 uL (Part A) of each calibration standard. Tabulate peak area responses against the concentration. The results are used to prepare calibration curves using a linear least squares fit for each analyte. Acceptable calibration curves are confirmed after reviewing the curves for linearity and passing the criteria for the initial calibration check standard. Alternately, if the ratio of response to concentration (response factor) is constant over the LCR (indicated by < 15% relative standard deviation (RSD)), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

i. Peak areas strongly recommended since they have been found to be more consistent, in terms of quantitation, than peak heights. Peak height can tend to be suppressed as a result of high levels of common anions in a given matrix which can compete for exchange sites. Using peak areas, it is the analyst responsibility to review all chromatograms to insure accurate baseline integration of target analyte peaks since poorly drawn baselines will more significantly influence peak areas than peak heights.

D. Once the calibration curves have been established they must be verified prior to conducting any sample analysis using an initial calibration check standard. This verification must be performed on each analysis day or whenever fresh eluent has been prepared. A continuing calibration check standard must be analyzed after every tenth sample and at the end of the analysis set as an end calibration check standard. The response for the initial, continuing and end calibration check must satisfy the QC criteria. If during the analysis set, the response differs by more than the calibration verification criteria, or the retention times shift more than ±5% from the expected values for any analyte, the test must be repeated, using fresh calibration standards. If the results are still outside these criteria, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable calibration check standard must be reanalyzed.

i. Control limits for calibration verification

Concentration range	Percent Recovery Limits
MRL to 10xMRL	75 – 125%
10xMRL to highest calibration level	85 – 115%

a. These control limits only apply if the MRL is established within a factor of 10 times the MDL. Otherwise, the limits are set at 85% to 115%.

F. After satisfying the requirements, the levels selected for the other calibration check standards should be varied between a middle calibration level and the highest calibration level.

6. PROCEDURE

A. Other columns, chromatographic conditions, or detectors may be used if the requirements of the QC section are met.

B. Check system calibration daily and, if required, recalibrate as necessarily.

C. Sample Preparation

i. For refrigerated or samples arriving to the laboratory cold, ensure the samples have come to room temperature prior to conducting sample analysis by allowing the samples to warm on the bench for at least 1 hour.

D. Using a Luer lock, plastic 10 mL syringe, withdraw the sample from the micro beaker and attach a 0.45 um particulate filter (demonstrated to be free of ionic contaminants) directly to the syringe. Filter the sample into an autosampler vial.

E. Using a 4 mm column, inject 50 uL of each sample. Tabulate peak area responses against the concentration. During this procedure, retention times must be recorded. Use the same size loop for standards and samples. Record the resulting peak size in area units. An automated constant volume injection system may also be used.

F. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

G. If the response of a sample analyte exceeds the calibration range, the sample may be diluted with an appropriate amount of reagent water and reanalyzed. If this is not possible then three new calibration concentrations must be employed to create a separate high concentration curve, one standard near the estimated concentration and the other two bracketing around an interval equivalent to ±25% the estimated concentration. The latter procedure involves significantly more time than a simple sample dilution therefore; it is advisable to collect sufficient sample to allow for sample dilution or sample reanalysis, if required.

H. Shifts in retention time are inversely proportional to concentration. Nitrate, phosphate and sulfate will exhibit the greatest degree of change, although all anions can be affected. In some cases this peak migration may produce poor resolution or make peak identification difficult.

I. Should more complete resolution be needed between any two coeluting peaks, the eluent can be diluted. This will spread out the run, however, and will cause late eluting anions to be retained even longer. The analysts must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria.

i. Eluent dilution will reduce the overall response of an anion due to chromatographic band broadening which will be evident by shortened and broadened peaks. This will adversely effect the MDLs for each analyte.

7. **DATA ANALYSIS AND CALCULATIONS**

A. Prepare a calibration curve for each analyte by plotting instrument response, as peak area, against standard concentration. Compute sample concentration by comparing sample response with the standard curve. If a sample has been diluted, multiply the response by the appropriate dilution factor.

B. Report ONLY those values that fall between the lowest and the highest calibration standards. Samples with target analyte responses exceeding the highest standard should be diluted and reanalyzed. Samples with target analytes identified but quantitated below the concentration established by the lowest calibration standard should be reported as below the minimum reporting limit (MRL).

C. Report results for Part A anions in mg/L.

D. Report NO_3^- as N

Traceability

A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date, date opened, and the logbook where information is recorded. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

IX. INSTRUMENT INFORMATION

Analyst should confirm the following:

1. Start Up routine for instrument is as follows:

a. Turn Power on to autosampler, conductivity detector, eluent generator and pump in any order.

b. Turn on the Helium gas supply~ 80 to 100. Ensure gas lines to bottles not in use are off. Ensure air supply to the injection valve is on.

c. Close the vent valves on sparging bottles and allow head pressure to build for a few moments. DI H2O bottles should be 7 to 10 psi.

d. Open the eluent supply valve(s) for the bottles in use. Check for sputter after eluent flow has started.

e. Load the autosampler cartridges and put autosampler into RUN state.

f. To vent airlocks, Run eluent with pump on and SRS off, open waste valve-> bottom door top black knob, just for a few seconds and close it.

g. Turn on the SRS power. NOTE: NEVER TURN ON THE SRS POWER SUPPLY WITHOUT THE PUMP GOING FIRST!!! Use either LOCAL/DIRECT CONTROL to enter commands at keypads, or REMOTE/DIRECT CONTROL to use the direct control option from the RUN menu within PEAKNET.

h. After System has come to equilibrium, load sequence and run.

2. Shut Down routine for instrument is as follows:

a. If the instrument is not going to be operated for a period of time, run deionized water through the eluent lines for ~ 30 minutes to an hour to rinse the lines.

b. Stop the OFF/ON pump and then select SRS-OFF.

c. Close gas supply valves and eluent valves on the eluent bottles. Turn off He supply. Is not necessary to vent the eluent bottles.

d. Power down the modules in any order.

3. General Sample Loading and Run Set-up.

a. Enter Peak-net Software from Desktop.

b. Loading a Run: Click on Schedule. The headings within the Schedule Editor are SAMPLE, SAMPLE TYPE, LEVEL, METHOD and DATA FILE.

i. Name each sample under the SAMPLE heading column. (ICB, ICV, LCSW, ICCS, IPC, sample #'s, etc.)

ii. SAMPLE TYPE is sample unless loading a calibration curve.

iii. LEVEL designations are used only when assigned to a calibration curve.

iv. **Enter method name under METHOD heading. In most cases, date of most recent calibration in Anions Method file will be used.**

v. **Enter the date under the DATA FILE heading. The program will then sequentially assign the data file names based on the date.**

vi. **All other column headings are defaulted to enter "1". Samples requiring dilution should be left at "1" and manual calculation is required.**

vii. **To include a command to Shut Down the pump at the end of the run: Name the row following the last sample, Pump Off under the sample heading. It is not necessary to include a vial in the corresponding position in the autosampler. Sampe type is Sample, and Method is entered as <pumpoff.met>.**

Typical run-log:

1	Blank
2	RLS@ 0.05/0.05ppm
3	ICV @ 2.5/25ppm
4	ICB
5	RLS @0.5ppm SO_4
6	LCSW ISA.....
7	Sample (Cl, SO_4....)
8	Sample (Cl, SO_4....)
9	Sample (Cl, SO_4....)
10	Sample (Cl, SO_4....)
11	Sample @ 10X(Cl)
12	Sample @ 50X(Cl)
13	CCV @ 2.5/2ppm
14	CCB
15	Sample (Cl, SO_4....)
16	Sample MS
17	Sample MSD
18	Sample (Cl, SO_4....)
19	Sample @ 10X (Cl)
20	Sample (Cl)
21	Sample (Cl, SO_4....)
22	Sample (Cl, SO_4....)
23	CCV @ 2.5/25ppm
24	CCB
25	Sample (Cl, SO_4....)
26	Sample (Cl, SO_4....)
27	Sample (Cl, SO_4....)
28	Sample (Cl, SO_4....)
29	Sample (Cl, SO_4....)

30	**Sample MS**
31	**Sample MSD**
32	**Sample (Cl, SO_4....)**
33	**CCV @5.0/50ppm**
34	**CCB**
35	**Sample (Cl, SO_4....)**
36	**Sample (Cl, SO_4....)**
37	**Sample (@ 2X (SO_4)**
38	**CCV @ 5.0/50ppm**
39	**CCB**
40	**pumpoff**

c. Save a schedule under File/Save as, using the date as the title of the Schedule.

d. When saved, exit out of Schedule Editor.

e. Load autosample cartridges in the same order as the scheduled run. After putting the cartridges in the autosampler, switch the autosampler to RUN using the Hold/Run button.

f. Assuming that the Pump is equilibrated with steady eluent baseline/uniform conductivity, enter into the RUN page.

g. Go to File to Open Method. Open correct method <date> of most recent calibration. This will begin pumping eluent at 1.0 mL/minute and turn on the SRS pump at 300 *u*amps voltage.

h. Next, go to file to Open Schedule. Open newly created schedule for the day.

i. When Method and Schedule are opened, go to Run and click on Start. The autosampler will inject into the first sample and the run should continue until completion.

X. POLLUTION PREVENTION

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

B. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

C. For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

XI. WASTE MANAGEMENT

A. The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel," available from the American Chemical Society at the address listed in Section 14.3 from method 300.1.

XII. CORRECTIVE ACTIONS

A. INSTRUMENT RELATED

1. ICV not within ± 10%

    a. If the problem is with the solution.

        i. Reprepare, obtain new stock if necessary.

    b. If the problem is with the calibration. Recalibrate thru analysis of appropriate standards and recheck ICV.

2. CCV not within ± 10%

    a. If the problem is with the solution.

        i. Reprepare, obtain new stock if necessary.

    b. If the problem is with the calibration.

        i. Recalibrate thru analysis of appropriate standards and reprepare/reanalyze the previous ten sample according the following guidelines.

            a. If the CCV was biased high, any of the previous ten samples which were BMDL do not require reanalysis.

b. If the CCV was biased low, the previous ten samples must be reanalysed.

3. CCB not >+_MDL (USACE)(**For DOD QSM Ver. 3 no analyte detected >2xMDL, frequency- beginning and ending a run and every 10 samples**)or ± RL or CRDL for others and CLP

   a. If the CCB is biased high.

      i. Any samples BDL or greater than 10X the CCB bias need not be reanalyzed.
      ii. Any samples above the detection limit but less than 10X the CCB level must be reanalyzed after the problem is corrected.

   b. If the CCB is biased low.

      i. Any samples greater than 10X the absolute CCB bias need not be reanalyzed.
      ii. All other samples must be reanalyzed after the problem is corrected.

4. LCS not within our in-house generated control limits (or ±20%).

   a. If the problem is with the instrument.

      i. Reanalyze when instrument is in control.

      ii. If biased high, the impact upon the data user must be evaluated. The samples will be re-extracted or the data will be qualified on the final report.

C. SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20%

   i. The associated sample data must be qualified on the final report.

2. Spike analysis recovery not within ±25%

   i. If the analyte level in the sample is greater than 4X the spiking level, the %recovery can not be evaluated and no action is taken.

   ii. If the analyte level in the sample is not greater than 4X the spiking level, the associated sample data must be qualified on the final report.

XIII. SOURCES/REFERENCES:

1. Standard Methods for the Examination of Water and Wastewater, Method 4110B, "Anions by Ion Chromatography", 18th Edition of Standard Methods (1992).

2. Dionex, System DX500 Operation and Maintenance Manual, Dionex Corporation, Sunnyvale, California 94086, 1996.

3. Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, Decemvber, 1981.

4. American Society for Testing and Materials. Test Method for Anions in Water by Chemically – Suppressed Ion Chromatography D4327-91. Annual Book of Standards, Vo. 11.01 (1993).

5. Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B; MDL determination.

6. Hautman, D.P. & Bolyard, M. Analysis of Oxyhalide Disinfection By-products and other Anions of Interest in Drinking Water by Ion Chromatography. Jour. Of Chromatog., 602, (1992), 65-74.

7. USEPA Methods 300.0; *Method for Determination of Inorganic Substances*(EPA/600/R-93/100) / *Method for the Determination of Organic and Inorganic Compounds in Drinking Water* (Vol. 1, EPA 815-R-00-014).

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):	
Batch Number(s):	
Method:	**EPA 300.0 Anions by Ion Chromatography**
Instrument is a Dionex DX-500 system. Equipped with Guard Column, Analytical Column, Conductivity Suppressor, Conductivity Detector, and Eluent Generator.	

QA/QC Item	Yes	No	NA	Second Level Review
1. Were samples analyzed within USACE holding times?				
2. Was initial calibration curve QC criteria met?				
3. Was all continuing calibration criteria in control?				
4. Did any sample exceed the highest calibration standard? (If yes, were appropriate dilutions made to generate samples concentration within calibration range?)				
5. Did RLS meet control limits?				
6. Did LCS, Laboratory Fortified Blank or blank spike meet control limits?				
7. Did MS/MSD meet control limits?				
8. Was the Blank below the project required detection limits?				
9. Did you return samples back to cold storage immediately after use?				
10. Were samples analyzed for Nitrate done within the 48-hr holding time?				
11. Sample preparation information is correct and complete.				
12. Were all samples filtered through a 0.45*u*m filter?				
13. Analytical results are correct and complete.				
14. The appropriate SOP's have been used and followed.				
15. Raw data" including all manual integration's have been correctly interpreted.				
16. "Special" sample preparation and analytical requirements have been met.				

ANALYST DATA REVIEW CHECKLIST
EPA 300.0 (Anions by IC)

17. Documentation complete (e.g., all anomalies in the analytical sequence have been documented, corrective action forms are complete. _____ _____ _____ _____

Comments on any "No" response:

_____

_____

_____

_____

_____

_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

TOTAL ALKALINITY , CARBONATE, BICARBONATE

METHOD
USEPA 310.1, SM2320B

SOP NUMBER: SOP-154

REVISION NUMBER: 2

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 11/28/06

DATE OF LAST REVIEW: 11/28/06

TOTAL ALKALINITY, CARBONATE, BICARBONATE
Method EPA 310.1 & Standard Methods 2320B

I. SCOPE AND APPLICATION

A. This method is applicable to drinking, surface, and saline waters, and domestic and industrial wastes.

B. The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 10 mL.

II. SUMMARY OF METHOD

An unaltered sample is titrated to an electrometrically-determined endpoint of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way. The calculation for total alkalinity (in calculation section of this SOP) is then used to calculate.

When the sample is being analyzed for phenolthalein alkalinity, carbonate, bicarbonate and total alkalinity, method 2320B is used. With this method, an unaltered sample is titrated to an electrometrically-determined endpoint of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way. The sample is then titrated to a pH exactly 0.3 pH units lower and the calculation for 2320B (in calculation section of this SOP) is used to calculate the samples for phenolthalein alkalinity, total alkalinity, carbonate and bicarbonate results. See note at the end of section VIII (Procedure) after step N for samples with pH greater than 8.3.

III. DEFINITIONS

1. **Preparation Blank (PB)-** Laboratory reagent water that is treated exactly as a sample including exposure to all glassware, equipment (pH probe) and reagents that are used with other samples. The PB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus.

2. **Laboratory Control Sample (LCS)-** An aliquot of reagent water or other blank matrices to which known quantities of the method anlayte is added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to to determine whether the

methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. The LCS is given a unique identifier so that it is traceable to its source and concentration and expiration date.

3. **Analysis Batch-** An analysis batch is a group of twenty field samples, a preparation blank, a laboratory control sample and a sample and/or laboratory control sample duplicate.

4. **Sample Duplicate-** Two sample aliquots, taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analysis of sample one and sample two indicate precision associated specifically with the laboratory procedures, removing any associated variables attributed by sample collection, preservation, or storage procedures.

5. **Method Detection Limit (MDL)--** The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

6. **Performance Evaluation Sample (PE)--** A certified solution of method analytes whose concentration is unknown to the analyst. Often, an aliquot of this solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used to determine statistically the accuracy and precision that can be expected when a method is performed by a comptetent analyst.

IV. SAMPLE HANDLING AND PRESERVATION

A. No preservation necessary except to keep chilled to 4°C until sample is analyzed. Do not open sample bottle until analysis.

B. The holding time for these samples is 14 days. Example: If sampled on November 1 at 10 a.m., analysis must be performed by November 14 at 10 a.m.

V. INTERFERENCES

A. Substances, such as salts or weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.

B. For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9, using the procedure in *Annual Book of ASTM Standards*, Part 31, "Water," p. 115, D-1067, Method D (1976).

C. Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.

VI. EQUIPMENT/APPARATUS

A. pH meter that uses a glass electrode and can be read to 0.01 pH units. The analyst will note on the data which pH meter (either the Corning 240 or Orion 420A) is used.

B. 250 mL beakers with wide enough mouths to allow room for burette tip and pH probe.

C. 10 mL Class A microburette.

VII. REAGENTS

A. Sodium carbonate solution, approximately 0.05N: Place 2.5 $\pm$0.2 g (to nearest mg) Na_2CO_3 (dried at 250°C for 4 hours and cooled in desiccator) into a 1-liter, Class A, volumetric flask and dilute to the mark. The Na_2CO_3 solution must be disposed of after one week.

B. Standard Acid (sulfuric or hydrochloric), 0.1N (high titrant): Dilute 3.0 mL concentrated H_2SO_4 or 8.3 mL concentrated HCl to 1 liter with distilled water. Dilute 40 mL of 0.05N Na_2CO_3 solution to 100 mL with deionized water and titrate potentiometrically with the Standard Acid to a pH of about 5. Lift electrode and rinse into beaker. Boil solution gently for 3 to 5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH Inflection point (3 units lower). This standardization must be done at least every three months. Calculate normality using:

$$N = \frac{A \times B}{53.00 \times C}$$

where: A = g Na_2CO_3 weighed into 1 liter
B = mL Na_2CO_3 solution
C = mL acid used to inflection point

C. Standard Acid (sulfuric or hydrochloric), 0.2N (low titrant): Dilute 200.0 mL of 0.1000 N Standard Acid to 1 liter with distilled water. Standardize by potentiometric titration of 15.0 mL 0.05N Na_2CO_3 solution every three months as above.

VIII. PROCEDURE

A. Write down time test started.

B. Fill 10 mL microburette with Standard Acid.

C. Pick titrant according to estimated total alkalinity. For example, a drinking water sample would probably use the 0.0200N titrant and a wastewater sample would probably use the 0.1000N titrant. Historical data is very useful for this.

A sample size of 50 mL is usually appropriate. If you use less than 1 mL of your high titrant, then you must titrate a new sample using low titrant. Using less than 1 mL of your low titrant is valid.

D. Sample size should be such that a sufficiently large volume of titrant is used (1 to 10 mL titrant).

E. Standardize and calibrate the pH meter according to laboratory procedures as explained. Using the Corning 240 pH meter, first calibrate the meter by putting the probe (which has been filled with the correct filling solution) in 7 buffer, setting the pH at 7; then in 4 buffer, setting the pH at 4, and then checking 7 again to make sure it still reads 7, if an adjustment is made to the 4 buffer then check that buffer again as well. The calibration buffers must be within ±0.05 pH units of the true value. Then check the 10 buffer. The reading should be within ±0.10 pH units. If not, recalibratin is necessary. Record this information in the appropriate log book. If automatic temperature compensation is not provided, make titration at 25 ±2°C. Check the buffer every 3 hous after calibration. The reading should be within ±0.20 pH units.

F. Carefully pour 50 mL or less into selected glass vessel by gently pouring down the side of the vessel so as to have the least aeration to sample as possible. Place a small magnetic stirring bar in vessel and start magnetic stirrer at medium to slow stirring.

Note: Where sample volume is adequate when using low titrant, a sample volume of 100 to 200 mL should be used and titration should be performed using a 10 mL microburette.

G. Place pH probe (which has been rinsed with DI water and patted dry with a Kimwipe) in the sample such that the probe tip is not touching the sides or bottom of the flask or beaker. If the probe has a protective cover, this is not a consideration.

H. Make sure there are no air bubbles at the bottom of filled burette. Wipe tip of burette so that no extra drops are clinging to it. Place tip of burette into mouth of vessel so that it is above the surface of the sample but is not touching the sides of the flask and drops can go nowhere but into the sample (e.g., drops from burette are not going onto pH probe or walls of flask but directly into sample).

I. Titrate a blank and an LCS first. This will let you know that the normalities of titrant are correct. If the result is out of the acceptable range of the LCS, run a duplicate LCS. If still out of range, find another second source and if still incorrect, restandardize titrant. First double-check titrant normality.

J. Record sample pH after reading is stable for 5 to 10 seconds.

K. Titrate sample to pH 4.5. This must be done slowly so as not to miss the exact pH. Record titrant volume.

L. The minimum titrant volume to be employed using low or high titrant is 1 mL. If high titrant is being used, go to low titrant; if low titrant doesn't work, use more sample. Be aware of sample volume that may be needed for other analyses. Do not dilute.

M. When titrating the sample, be sure to allow time for the pH to equilibrate so that the inflection point will not be passed.

N. Place pH probe in 7 buffer between samples. If this does not read 7, recalibrate between 4 and 7.

O. Potentiometric titration of low alkalinity

   a. For alkalinity of < 20 mg/L titrate 100 – 200 mL as above using a 10 mL microburet and 0.02 N acid solution.
   b. Stop titration at pH in range of 4.3-4.7, record volume and exact pH. Very carefully add titrant to lower pH exactly 0.3 pH units and record volume. See note below.

Note : For method 2320B, if the pH of the sample is above 8.3, the sample needs to be titrated for phenolthalein alkalinity, first check original pH. If it is not above 8.3, the phenolthalein result will be below the minimum detection limit. If the original pH is above 8.3, titrate sample as in above procedure but down to 8.3 instead of 4.5, and record titrant volume in box A on the alkalinity bench sheet. Then proceed with the regular procedure titrating to pH 4.5, and recording this result in box B on the alkalinity bench sheet, then carefully titrate exactly 0.3 pH units lower to pH 4.2 and record titrant volume at this level, in box C on the alkalinity bench sheet.

IX. CALCULATIONS

The detection limit is 1.0 mg/L $CaCO_3$.

Potentiometric titration to pH 4.5

$$\text{Total Alkalinity mg/ L } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{mL of Sample}}$$

Where: A = mL Standard Acid to pH 4.5
N = Normality Standard Acid

Potentiometric titration of low alkalinity = T below

Method 2320B calculations

Use the following notation in below calculations:

P = Phenolthalein alkalinity
T = Total alkalinity

$$P = \frac{A \times N \times 50{,}000}{\text{mL of Sample}} \qquad T = \frac{(2B-C) \times N \times 50{,}000}{\text{mL of Sample}}$$

If P	= 0	Carbonate	= 0	Bicarbonate	= T
If P	< 1/2T	Carbonate	= 2P	Bicarbonate	= T-2P
If P	= 1/2T	Carbonate	= 2P	Bicarbonate	= 0
If P	> 1/2T	Carbonate	= 2(T-P)	Bicarbonate	= 0
If P	= T	Carbonate	= 0	Bicarbonate	= 0

Where: A = mL titrant to pH 8.3
B = mL titrant to pH 4.5
C = mL titrant to pH 4.2
N = normality Standard Acid

X. QUALITY CONTROL

A. Run a laboratory control sample (LCS) for each batch of samples (maximum of 20 samples per day). If the LCS does not fall in the range of 80 to 120%, corrective action must be taken to find the problem and correct it.

B. Run a preparation blank (PB) for each batch of samples (maximum of 20 samples per day). The PB should be less than the reporting limit.

C. Analyze a sample duplicate every 10 to 20 samples (depending on specific client requirements). Relative percent difference (RPD) on duplicates should be less than 20%.

D. The Excel file for calculations is located in "V:\WCM\TESTS\ALK&CARB\".

E. Calculate all percent recoveries and relative percent differences on duplicates and show calculations on data.

Calculate spikes as follows where everything is in concentration.

$$\% \text{ Recovery} = \frac{\text{Spike} - \text{Sample}}{\text{True Value}} \times 100$$

Relative percent difference is calculated as follows, with everything in concentration:

$$\text{RPD} = \frac{\text{Higher Concentration} - \text{Lower Concentration}}{\text{Average of Concentrations}} \times 100$$

XI. CORRECTIVE ACTION

A. If the preparation blank is higher than the reporting limit, all samples less than ten times the concentration of the blank must be reanalyzed.

B. If the laboratory control sample (LCS) is out of the range of 80 to 120%, and the % recovery is high (higher than 120%), only sample concentrations less than the reporting limit are acceptable data. Otherwise, all data with concentrations above the method detection limit must be reanalyzed with an LCS in the range of 80 to 120%. If the LCS is low (less than 80%), all samples must be reanalyzed.

C. If the relative percent difference (RPD) between the sample and the sample duplicate are out of the range of 20%, the sample should be repeated one more time to make sure that the problem is not caused by analyst's error. If the RPD is still higher than 20% the sample is flagged on the final report with a "*".

XII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIII. SAFETY

A. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential heath hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

B. Your laboratory manager and/or Safety Officer is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. A formal safety plan is also available. Use proper personal protection equipment, PPE, such as safety glasses, gloves and laboratory coats should be warn when handling samples and chemicals.

XIV. METHOD PERFORMANCE

A. Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

		Accuracy as	
Increment as Alkalinity mg/L, CaCO3	Precision as Standard Deviation mg/L, CaCO3	Bias, %	Bias, mg/L, CaCO3
8	1.27	+10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	-8.19	-9.3
119	5.36	-7.42	-8.8

XV. REFERENCES

A. Methods for the Chemical Analysis of Water and Wastes, EPA Series Method 310.1.

B. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p.278, method 403, (1975).

C. Standard Methods for the Examination of Water and Wastewater, 18th Edition, p. 2-26, method 2320B, (1992).

Empirical Laboratories, LLC

TURBIDITY

METHOD 180.1 (NEPHELOMETRIC)

SOP NUMBER: SOP-158

REVISION NUMBER: 2

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 01/08/03

DATE OF LAST REVIEW: 01/28/06

TURBIDITY
Method 180.1 (Nephelometric)

I. SCOPE AND APPLICATION

This method is applicable to drinking, surface, and saline waters in the range of turbidity from 0 to 40 nephelometric turbidity units (NTU). Higher values may be obtained with dilution of the sample.

Note 1: NTU's are considered comparable to the previously reported Formazin Turbidity Units (FTU) and Jackson Turbidity Units (JTU).

Note 2: Turbidity analyses is used to determine the necessity for digestion for total metals. Drinking Water, Clean Water Act and liquid waste sample matrices must have turbidity <1.0 NTU for undigested total metal analyses by Atomic Absorption or Inductively Coupled Plasma Spectroscopy. All samples with turbidity >1.0 NTU must be digested prior to total metal determination.

II. SUMMARY OF METHOD

The method is based upon a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings, in NTU's, are made in a nephelometer designed according to specifications outlined in Apparatus. A standard suspension of Formazin, prepared under closely defined conditions, is used to calibrate the instrument.

Formazin polymer is used as the turbidity reference suspension for water because it is more reproducible than other types of standards previously used for turbidity standards.

A commercially available polymer standard is also approved for use for the National Interim Primary Drinking Water Regulations. This standard is identified as AMCO-AEPA-1 available from Amco Standard International, Inc.

III. SAMPLE HANDLING AND PRESERVATION

Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.

IV. INTERFERENCES

A. The presence of floating debris and coarse sediments which settle out rapidly will give low readings. Finely divided air bubbles will affect the results in a positive manner.

B. The presence of true color, that is the color of water which is due to dissolved substances which absorb light, will cause turbidities to be low, although this effect is generally not significant with finished waters.

V. APPARATUS

A. The turbidimeter shall consist of a nephelometer with light source for illuminating the sample and one or more photo-electric detectors with a readout device to indicate the intensity of light scattered at right angles to the path of the incident light. The turbidimeter should be so designed that little stray light reaches the detector in the absence of turbidity and should be free from significant drift after a short warmup period.

B. The sensitivity of the instrument should permit detection of a turbidity difference of 0.02 unit or less in waters having turbidities less than 1 unit. (We do not measure turbidity if the concentration is <1.0. This is our detection limit.) The instrument should measure from 0 to 40 units turbidity. Several ranges will be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities.

C. The sample tubes to be used with the available instrument must be of clear, colorless glass. They should be kept scrupulously clean, both inside and out, and discarded when they become scratched or etched. They must not be handled at all where the light strikes them, but should be provided with sufficient extra length, or with a protective case, so that they may be handled.

D. Differences in physical design of turbidimeters will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, the following design criteria should be observed:

1. Light source: Tungsten lamp operated at a color temperature between 2200 and 3000°K.

2. Distance traversed by incident light and scattered light within the sample tube: Total not to exceed 10 cm.

3. Detector: Centered at 90° to the incident light path and not to exceed ±30° from 90°. The Detector, and filter system if used, shall have a spectral peak response between 400 and 600 nm.

E. The Hach Turbidimeter, Model 2100 and 2100A, is in wide use and has been found to be reliable; however, other instruments meeting the above design criteria are acceptable.

VI. REAGENTS

A. Turbidity-free water: Pass distilled water through a 0.45µ pore size membrane filter if such filtered water shows a lower turbidity than the distilled water. We normally use unfiltered DI.

B. Stock Formazin Turbidity Suspension:

1. Solution 1: Dissolve 1.0 g hydrazine sulfate, $(NH_2)_2oH_2SO_4$, in distilled water and dilute to 100 mL in a volumetric flask.

2. Solution 2: Dissolve 10.0 g hexamethylenetetramine in distilled water and dilute to 100 mL in a volumetric flask.

3. In a 100 mL volumetric flask, mix 5.0 mL Solution 1 with 5.0 mL Solution 2. Allow to stand 24 hours at 25 ±3°C, then dilute to the mark and mix.

C. Standard formazin turbidity suspension: Dilute 10.0 mL stock turbidity suspension to 100 mL with turbidity-free water. The turbidity of this suspension is defined as 40 units. Dilute portions of the standard turbidity suspension with turbidity-free water as required.

D. A new stock turbidity suspension should be prepared each month. The standard turbidity suspension and dilute turbidity standards should be prepared weekly by dilution of the stock turbidity suspension.

E. The AMCO-AEPA-1 standard as supplied requires no preparation or dilution prior to use.

VII. PROCEDURE

A. Turbidimeter calibration: The manufacturer's operating instructions should be followed. Measure standards on the turbidimeter covering the range of interest. If the instrument is already calibrated in standard turbidity units, this procedure will check the accuracy of the calibration scales. At least one standard should be run in each instrument range to be used. Some instruments permit adjustments of sensitivity so that scale values will correspond to turbidities. Reliance on a manufacturer's solid scattering standard for setting overall instrument sensitivity for all ranges is not an acceptable practice unless the turbidimeter had been shown to be free of drift on all ranges. If a pre-calibrated scale is not supplied, then calibration curves should be prepared for each range of the instrument.

B. Turbidities less than 40 units: Shake the sample to thoroughly disperse the solids. Wait until air bubbles disappear than pour the sample into the turbidimeter tube. Read the turbidity directly from the instrument scale or from the appropriate calibration curve.

C. Turbidities exceeding 40 units: Dilute the sample with one or more volumes of turbidity-free water until the turbidity falls below 40 units. The turbidity of the original sample is then computed from the turbidity of the diluted sample and the dilution factor. For example, if five volumes of turbidity-free water were added to one volume of sample, and the diluted sample showed a turbidity of 30 units, then the turbidity of the original sample was 180 units.

   The Hach Turbidimeters, Models 2100 and 2100A, are equipped with five separate scales: 0 to 0.2, 0 to 1.0, 0 to 100, and 0 to 1000 NTU. The upper scales are to used only as indicators of required dilution volumes to reduce readings to less than 40 NTU.

Note: Comparative work performed in the MDQAR Laboratory indicates a progressive error on sample turbidities in excess of 40 units.

Empirical Laboratories, LLC

VIII. CALCULATIONS

A. Multiply sample readings by appropriate dilution to obtain final reading.

B. Report results as follows:

NTU	Record to Nearest:
0.0 - 1.0	0.05
1 - 10	0.1
10 - 40	1
40 - 100	5
100 - 400	10
400 - 1,000	50
>1,000	100

IX. PRECISION AND ACCURACY

A. In a single laboratory (EMSL), using surface water samples at levels of 26, 41, 75, and 180 NTU, the standard deviations were $\pm$0.60, $\pm$0.94, $\pm$1.2, and $\pm$4.7 units, respectively.

B. Accuracy data are not available at this time.

X. REFERENCES

1. *Annual Book of ASTM Standards*, Part 31, "Water," Standard D1889-71, p. 223 (1976).

2. *Standard Methods for the Examination of Water and Wastewater*, 14th Edition, p. 132, Method 214A (1975).

DISTILLATION OF AQUEOUS/SOLID SAMPLES FOR TOTAL AND NON-AMENABLE CYANIDE ANALYSIS

METHODS 335.1/335.4/(SW846) 9012A/USEPA CLP ILMO 4.1 (NJDEP does not accept CLPILM 04.1 after June, 2003) Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

SOP NUMBER: SOP-164

REVISION NUMBER: 12

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 11/29/06

DATE OF LAST REVIEW: 11/29/06

DISTILLATION OF CYANIDE, TOTAL AND AMENABLE

REFERENCE:
SW846 METHOD 9012A, USEPA Methods 335.1, 335.4, CLP ILMO 4.1
See Addendum for USEPA CLPILM 05.2 (Aqueous, Soil/Sediment)

I. SCOPE AND APPLICATION

A. This method is applicable to the distillation of cyanide from drinking, surface, and saline waters, domestic and industrial wastes, and soil/sediments.

B. The limit of detection for waters is 0.0050 mg/L and the limit of quantitation is 0.010 mg/L. The limit of detection for soils is 0.13 mg/kg and the limit of quantitation is 0.25 mg/kg.

II. SUMMARY OF METHOD

A. The cyanide as hydrocyanic acid is released from cyanide complexes by means of a reflux distillation operation, and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

B. Cyanide is defined as cyanide ion (CN^-) and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

III. SAMPLE HANDLING AND PRESERVATION

A. The sample should be collected in plastic or glass bottles of 100 mLs. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.

B. Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.06 g of ascorbic acid for each liter of sample volume.

C. Samples (not including soils/sediments) must be preserved with 2 mL of ten normal sodium hydroxide per liter of sample (pH $\geq$12) at time of collection.

D. Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator to maintain temperature at 4°C.

E. The holding time for cyanide is 14 days counting the day of sampling as the first day. This applies for soils as well as waters. Samples must be distilled and analyzed within 14 days of sampling.

IV. INTERFERENCES

A. Interferences are eliminated or reduced by using the distillation procedure.

B. Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation, must be treated by adding lead acetate, or if the sulfide concentration is too high, add powdered lead carbonate [$Pb(CO_3)_2$] to avoid significantly reducing pH. Repeat test until a drop of treated sample no longer darkens the acidified lead acetate test paper. Filter sample before raising pH for stabilization.

C. High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN.

D. The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser.

V. SAFETY

A. **CAUTION: KCN is highly toxic. Avoid contact with standard solutions.**

B. If an alkaline solution containing simple cyanide is acidified, the simple cyanide will be released.

C. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential heath hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

D. Your laboratory manager and/or Safety Officer is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) are made available to all personnel involved in the chemical analysis. A formal safety plan is also available. Use proper personal protection equipment, PPE, such as safety glasses, gloves and laboratory coats should be warn when handling samples and chemicals.

VI. EQUIPMENT/APPARATUS

A. Reflux distillation apparatus such as shown in Figure 1. Midi distillation apparatus which uses Hammett Scientific Glassware Note: This glassware is made to fit our specific block digester for cyanide. Glassware orders must be made in advance since they are not made until ordered.

VII. REAGENTS AND STANDARDS PREPARATION

A. Reagents

1. **Sodium Hydroxide, 0.25N**: Dissolve 10 g grams of NaOH in DI water and dilute to 1 liter with DI water. Store in a labeled plastic container at room temperature.

2. **Sulfuric Acid 1:1:** Slowly add 500 mL of concentrated H_2SO_4 to 500 mL DI water. Use caution because solution will become extremely hot!! Allow to cool while continuing to stir. Store in a labeled container at room temperature.

4. **Magnesium Chloride Solution**: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1 liter flask; dissolve and dilute to 1 liter with DI water. Store in a labeled plastic container at room temperature.

5. **Chlorine Bleach Made with Sodium Hypochlorite**, such as Chlorox.

6. **Rhodanine Indicator**:
Dissolve 20 mg of p-dimethyl-amino-bensalrhodanine in 100 mL acetone.

7. **Sulfamic Acid:** Dissolve 40 g of sulfamic acid in DI water, dilute to 100 mL (saturated solution). **NOTE:** When making this reagent for use with the maxi-distillation system the 40 g of sulfamic are diluted to one liter with DI water

8. **Phenolphthalein solution:** Commercially prepared.

9. **Lead Acetate Test Paper**: Commercially prepared.

10. **Acetate Buffer Solution, pH 4.0:** Dissolve 146g anhydrous $NaC_2H_3O_2$, or 243 g $NaC_2H_3O_2.3H_2O$, in 400 mL distilled water, add 480 g conc. acetic acid, and dilute to 1 L with chlorine-demand-free water.

11. **Lead Acetate**

12. **Powdered Lead Carbonate [$Pb(CO_3)_2$]**

B. Standards

1. Traceability

a. A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

b. All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date and the logbook where information is recorded. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

c. The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

2. Preparation

a. Stock Cyanide Solution at 1000 mg/L: Commercially prepared.

b. Working Standard Cyanide Solution: Prepare fresh daily by diluting 5 mL of stock cyanide solution to 500 mL in a volumetric flask with 2 mL of 10N NaOH, with DI water. 1 mL - 10 µg CN. Record the preparation in the log book.

c. Performance Evaluation (PE) samples which we have analyzed and received true values for are used for the Laboratory Control Samples. These PE samples are given a unique identifier and all information such as expiration date (typically one year from the date made), source, concentration and preservation are recorded in the Inorganic Standards book A (ISA). The ISA # assigned is used to label this PE sample and is used on all data to trace it back to its source and true concentration.

VIII. CALIBRATION

A. Not applicable. See SOP-175 **"POST DISTILLATION ANALYSIS OF CYANIDE BY THE LACHAT"** for analysis.

IX. PROCEDURE

A. Pretreatment for cyanides amenable to chlorination

1. Two sample aliquots are required to determine cyanides amenable to chlorination. Place one 25 mL aliquot or a volume diluted to 25 mL, in a 100 mL beaker, under the hood, add a stirring bar, and place on a magnetic stirrer, and start stirring bar turning.

2. Check pH and adjust to between 11 and 12 units, with 1.25N NaOH. Use NaOH pellets if solution is highly buffered.

3. Add sodium hypochlorite chlorine bleach (Clorox) solution dropwise until a drop of well-mixed sample turns KI starch paper a distinct blue color. Add about 10 drops excess bleach. (Caution: the initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride.) Maintain this excess for one hour, continuing agitation. Check periodically during the hour (15 minute intervals) to make sure an excess is maintained. If necessary, add additional hypochlorite bleach solution. Also check the pH and adjust back up to 11 to 12 units if necessary.

4. After one hour, add 0.025 g portions of ascorbic acid until KI starch paper shows no residual chlorine. Add an additional 0.025 g of ascorbic acid to ensure the presence of excess reducing agent.

5. Turn off stirring plate and remove stirring bar. Proceed with distillation as in the procedure.

6. Test for total cyanide in both the chlorinated and unchlorinated aliquots. (The difference of total cyanide in the chlorinated and unchlorinated aliquots is the cyanide amenable to chlorination.)

B. Spikes and high and low check standards

1. **Spikes** are prepared from a secondary working standard. The 10 mg/L working standard is diluted 5 mLs to 50 mLs to make a 1 mg/L CN standard. This solution is prepared daily as needed. Pipette 2.5 mLs of this solution into 25 mLs of the sample to prepare a 0.10 mg/L spike.

2. **Low Distilled Check standard (low DCV).** Dilute 4.0 mL of the 10 mg/L working standard to 100 mLs in a volumetric flask. Then dilute 3.0 mLs of this solution to 25 mLs with DI water, to make a 0.048 mg/L standard.

3. **High Distilled Check standard (high DCV).** Dilute 0.5 mLs of the 10 mg/L working standard to 25mLs in a volumetric flask with DI water, to make a 0.20 mg/L standard.

C. Distillation

1. For Waters: Place 25 mL of sample, or an aliquot diluted to 25 mL, in a sample tube. 0.025 N NaOH must be used for all sample dilutions following the distillation.

2. For Soils or Sludges:

   a.) It is extremely important that waste (when appropriate), soil and sediment samples be mixed thoroughly to ensure that the sample is as representative as possible of the sample media. The most common method of mixing is referred to as quartering. The quartering procedure should be performed as follows:

   - The material in the sample pan(inorganic-plastic/organic-aluminum) should be divided into quarters and each quarter should be mixed individually.
   - Two quarters should then be mixed to form halves.
   - The two halves should be mixed to form a homogenous matrix.

This procedure should be repeated several times until the sample is adequately mixed.

NOTE: Samples that are clay type materials should be handled in a different manner. Due to these type sample matrices having an affinity to stick to most anything that touches it, another approach must be followed. Obtain a representative sub-sample aliquot from the center or middle section of the sample container.

b.) Accurately weigh a representative 1-g minimum (record actual weight) portion of wet-weight sample (unless there are project-specific requirements where a lower detection limit is required) and transfer it to a sample tube. Add 25 mL of 0.25 N NaOH. Shake or stir the sample so that it is dispersed.

3. Add one drop of Phenolphthalein solution to verify preservation. A positive test is indicated by a bright pink color. If not add a small amount of NaOH.

4. To test for sulfide, place a drop of sample on lead acetate paper, previously moistened with acetic acid buffer solution (pH 4). A positive test is indicated by a black color on the paper.

   a.) If positive the sample will need to be filtered through 934AH filter paper. (4.5cm size) The filtrate will be treated and the filter added back to the treated filtrate before distillation.

   b.) Treat filtrate with powdered lead carbonate [$Pb(CO_3)_2$]. Repeat test until a drop of treated sample no longer darkens the acidified lead acetate test paper.

   c.) Filter the resulting precipitate (should form a lead sulfide which will be black in appearance).

   d.) Once the filtrate is treated and filtered, the filter with the original solids from the pretreated sample will be added back to the treated filtrate and then distilled.

5. Add 25 mL of sodium hydroxide solution 0.25N to the absorber and assemble the apparatus as shown in Fig. 1.

6. Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum such that air bubbles from the thistle tube in the flask at a rate of 3 to 5 per second.

   Note: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It may be necessary to readjust the air rate occasionally to prevent the solution in the sample tube from boiling and spewing out through the thistle tube.

7. Turn on condenser water.

8. Add 0.5 mLs of sulfamic acid through the thistle tube.

9. Slowly add 2 mL 1:1 H_2SO_4 through the thistle tube.

10. Add 2 mL 2.5 M $MgCl_2$ through the thistle and rinse it down with deionized water.

11. Reflux at 100°C for 90 minutes.

12. Disconnect absorber and transfer the solution from the absorber into a storage container.

14. Record distillation information in the distillation log. Include date, analyst, sample number, client, matrix, position, sample mass / volume, distillation time, cool down time, when transferred to analyst, when analyzed.

X. CALCULATIONS

A. Sample volumes / masses must be recorded accurately in the distillation log to allow the analyst to correctly calculate the final concentration of cyanide correctly.

XI. DISTILLATION GLASSWARE CLEANING & LABELING

A. The distillation glassware is cleaned thoroughly with hot soapy water between distillations. 1:1 HCl is aerated through the frits on the block to ensure that the frits are clean. Deionized water is forced up through the glassware to rinse it. The cold fingers are dipped in mild acid, rinsed and wiped off.

B. All glassware must be labeled and each position's label must be recorded in the distillation log with the sample that was distilled in that particular vessel.

C. When sample concentrations are at or exceed 1000 mg/L a deionized water blank must be distilled in the exact glassware used for that sample before processing any other client's sample to ensure that the glassware is cleaned and has no residual cyanide to carryover.

XII. QUALITY CONTROL

A. With each distillation batch of samples (maximum of 20 samples) a preparation blank (PB) must be distilled.

B. Each distillation batch of aqueous samples **requires a laboratory control sample (LCS) each day or per 20 samples whichever is more frequent.** Under CLP the LCS serves as the distilled ICV.

C. With each distillation batch of soil samples a soil LCS **each day or per 20 samples whichever is more frequent.**

D. A high and low check standard (DCV/ICV) must be distilled each day or per 20 samples whichever is more frequent. A non-distilled check standard must be prepared daily. This will be used to verify the preparation of the DCV if the DCV results are outside the specification limits. Under CLP the aqueous LCS serves as the ICV.

E. A sample spike (MS) and sample spike duplicate (MSD) are performed with each set of twenty samples. CLP requires 1 duplicate and 1 spike per batch. All QC samples should be taken through the whole procedure including distillation. Spikes are added to the boiling flask in the same manner as standards adding 25 mL of samples or a dilution as used for the unspiked sample. Spike concentration is listed in the method. The addition of the spiking solution must be witnessed and such must be noted in the digestion log.

XIII. CORRECTIVE ACTION

A. If any problems, such as low or high recovery for check standards or LCSs occur, contact the Group Leader. Problems most frequently encountered (for the distillation procedure) are listed below.

B. Recoveries are affected in various ways.

1. If the spiking solution is not prepared properly (e.g., making the proper dilutions), the check standard will be out of control. Caution should be used in calculating the dilution and performing the pipetting.

2. Also, the air flow from the vacuum pumps can cause low recovery. Pay attention to the air flow (it should be in the area of 1 to 2 bubbles per second). If it is too great the HCN does not have an adequate amount of time to be absorbed by the NaOH solution.

3. If the heating block is not heating properly, this will also lead to low recovery. During the distillation, periodically check the sample tubes for the presence of heat (tubes should be very hot to the touch).

4. The addition of all reagents, including the spiking solution, is essential. Without the $MgCl_2$, 1:1 H_2SO_4, or spiking solution, the percent recovery will suffer greatly for complex cyanide. The recovery of simple cyanides will usually be unaffected.

5. If the volume of 0.25 N NaOH and reagent water is not accurate in the NaOH absorber tubes, low recoveries will usually occur.

B. Spike recoveries are affected in similar ways. Refer to the above suggestions. Also, if possible, do not spike a sample that is known to be high in cyanide. This may cause recovery and calculation problems.

XIV. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

The following is a list of changes for sample preparation when the 5.2 statement of work is required:

1. The ICV shall be distilled.

2. Boiling chips are to be added to each sample. Midi-Distillation is reflux 1.5 hours then the heat and vacuum is turned off and the samples cool an additional 15 minutes.

3. The QC criteria for both the Distillation Check QC and the distilled ICV is ±15%.

4. A CRI is required at the beginning and end of each run and for every 20 samples. The QC criteria for the CRI is ±30%.

5. Rounding rule for the appropriate level of precision is that the figure following those to be retained is ≥ 5, round up: otherwise round down. (examples: 1.5 and 2.5 would be 2 and 3 respectively rounded up; 1.4 and 2.4 would be 1 and 2 respectively rounded down) Please see Exhibit B, Section 3, (3.3.9.1) of SOW ILM0 5.2 for more guidance on rounding significant figures.

Empirical Laboratories, LLC

RESIDUE, NON-FILTERABLE TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS

USEPA METHOD 160.2 (GRAVIMETRIC, DRIED AT 103 TO 105°C

SOP NUMBER: SOP-174

REVISION NUMBER: 2

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: 01/04/02

DATE OF LAST REVIEW: 02/08/06

RESIDUE, NON-FILTERABLE
TOTAL SUSPENDED SOLIDS AND VOLATILE SUSPENDED SOLIDS
BY EPA METHOD 160.2 (Gravimetric, Dried at 103 to 105°C)

I. SCOPE AND APPLICATION

A.. This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

B. The practical range of the determination is 4 mg/L to 20,000 mg/L.

II. SUMMARY OF METHOD

A. A well-mixed sample is filtered through a glass fiber, and the residue retained on the filter is dried to constant weight at 103 to 105°C.

B. The filtrate from this method may be used for residue, filterable.

III. SAMPLE HANDLING AND PRESERVATION

A. Non-representative particulates such as leaves, sticks, fish and lumps of fecal matter, should be excluded from the sample if it is determined that their inclusion is not desired in the final result.

B. Refrigeration at 4°C to minimize microbiological decomposition of solids, is the only preservation needed.

C. The holding time for residue non-filterable is 7 days, analysis should begin within 2 days of receipt because of problems in the past with holding times and/or problems with the test that make reanalysis necessary.

IV. DEFINITIONS

Residue, non-filterable, is defined at those solids which are retained by a glass fiber filter and dried to constant weight at 103 to 105°C.

V. INTERFERENCES

A. Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.

B. Samples high in filterable residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any-dissolved solids in the filter minimizes this potential interference.

IV. EQUIPMENT/APPARATUS

A. Glass fiber filter discs, without organic binder, 934-AH or equivalent.

B. Filter holder or Gooch crucible adapter.

C. Suction flask, 1000 mL or more.

D. Gooch crucibles, porcelain made by Coors.

E. Buchner funnels

F. Drying oven, 103 to 105°C

G. Desiccator

H. Analytical balance, capable of weighing to 0.1 mg

I. Vacuum pump, see note on maintenance this procedure.

VII. CALIBRATION

A. The detection limit for TSS depends on volume use a volume of 1000 mL gives a detection limit of 1.0 ppm.

B. Calibrate analytical balance daily or as used by weighing a 1 gram and a 20 gram weight to check calibration. Record weight results.

C. Calibrate analytical balance monthly by checking the whole range of weights in reference standards weight set (borrow from Toxicology).

VIII. PROCEDURE

A. Crucible Prep:

1. Wash Gooch crucibles in hot soapy water, rinse with tap water, and then thoroughly inside out with D. I. water.
2. Set up a 1 liter suction flask with Gooch crucible adapter, apply vacuum, place a 3.4 cm 934-AH glass fiber filter wrinkled surface up in crucible and put crucible on holder, making sure filter covers all the holes in the bottom of the crucible. Wash the filter with three successive 20 mL volumes of distilled water. Make sure all traces of water have passed through, discard washings. This rinses the filter and also allows filter to be well seated in the Gooch crucible.

3. Place crucible in the 103 to 105°C oven until needed.

4. Make sure that desiccant in desiccator is placed in 104°C oven overnight to dry when the dessicant undergoes a color change.

5. When total non-filterable residue is to be run, that day place crucibles in Desiccator 1 hour and weigh on analytical balance recording weights under "tare weight" on solids sheet. After weighing, handle the crucible with filter with tongs only.

6. When a detection limit of 1.00 ppm is required by a client such as Automotive Components Holdings, LLC (001, MW) a 9.0 cm 934-AH filter disc is prepared by placing the filter in a clean buchner funnel and running three successive 50 mL volumes of D. I. water through the filter and continuing to apply vacuum after water has passed through until filter is completely dry.

7. Then place filter on an aluminum pan and place in 103 to 105°C oven for at least 1 hour. Then place filter on aluminum pan in desiccator for at least 1 hour. Weigh filter only, on analytical balance and record under tare weight for that sample. After weighing, handle filter with tongs only. Filter 1000 mL of sample through this filter, and place back on aluminum pan and then in the 103 to 105°C oven for 1 hour, then in the desiccator for 1 hour and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 1.0 mg.

B. Residue, Non-Filterable

1. Selection of sample volume.

   a. Attempt to use the most volume you can filter easily and still rinse with D. I. water after sample is filtered. Keep in mind that other tests may need to be run on the same sample you are getting TSS sample out of. Never use all the sample unless instructed to. Accidents do happen and you may need to repeat the test.

   b. If enough sample is available on samples that filter easily try to use at least 250 mL.

   c. On samples which filter slowly but leave no obvious residue on the filter, make sure you rinse these samples well with D.I. water because this indicates that they are high in dissolved solids.

   d. On samples which are marked mixed liquor suspended solids or MLSS use at least 10 mL of sample pipetting with a wide-bore pipet. These samples settle quickly and therefore must be shaken vigorously and pipetted quickly in order to get a representative sample. Samples such as these should also be rinsed well because they are usually high in dissolved solids.

   e. If you try to filter too much of a sample and it stops up the filter before all the sample is filtered start over with a new crucible, using less sample, never try to go with the volume filtered. Reason being that solids sample are measured into a graduated cylinder and start to settle out even before you start pouring the sample into the crucible to filter. This means you are not using a representative sample unless the whole volume poured up in the cylinder is used and the cylinder is washed with D.I. water with washings filtered through the same crucible.

2. Running Samples:

   a. Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the bottom of the crucible covering all the holes.

b. Shake the sample vigorously and quantitatively transfer the predetermined sample volume to the filter using a graduated cylinder or wide-bore pipette where necessary. Remove all traces of water by continuing to apply vacuum after sample has passed through.

c. With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three 25 mL portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

d. Remove the crucible/filter from crucible adaptor using tongs. Dry at least one hour at 103 to 105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less then 1.0 mg).

C. Volatile Suspended Solids.

After total non-filterable residue is run place same crucible with filtered sample in it in the furnace at 550 ±50°C for 15 minutes using tongs. Place in 103 to 105°C oven to cool about 10 minutes then put crucible in desiccator for 1 hour, and weigh.

IX. CALCULATIONS

A. Calculate total non-filterable residue as follows:

$$\text{TSS mg/L} = \frac{(A-B)\,1000}{\left(\frac{C}{1000}\right)}$$

Where: A = weight of dried residue + dish in grams.
B = weight of dish in grams.
C = volume of sample used in mL.

B. Calculate volatile non-filterable residue as follows:

$$\text{VSS mg/L} = \frac{(A-B)\,1000}{\left(\frac{C}{1000}\right)}$$

Where: A = weight of dried residue + dish in grams.
B = weight of dried residue at 550°C ±50°C + dish in grams
C = volume of sample used in mL.

X. QUALITY CONTROL

A. Do a duplicate every tenth sample.

B. Do a total suspended solids LCS at least once a week to check accuracy of analytical balance and drying ovens. If the first weighing result of the LCS is within specification limits, more weighings are not necessary.

NOTE: Regular maintenance must be done on the vacuum pump periodically. Always check oil holders to make sure oil is in it up to the red fill line before using. Make sure that reservoir is hooked up in line case water filters over. This reservoir should be hooked up such that any water coming over will be collected in a flask so it will not go directly into the pump itself. This reservoir should be dumped and cleaned periodically.

POST-DISTILLATION ANALYSIS FOR CYANIDE BY THE LACHAT METHODS 335.4;(SW846) 9012A USEPA-CLP 4.1 (NJDEP does not accept CLPILM 04.1 after June, 2003)

Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

SOP NUMBER: SOP-175

REVISION NUMBER: 9

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 07/18/06

DATE OF LAST REVISION: 07/18/06

POST DISTILLATION ANALYSIS OF CYANIDE BY THE LACHAT
0.005-0.500 mg CN^-/L

References:
USEPA METHOD 335.4/(SW846) 9012A/USEPA CLP ILMO 4.1
See Addendum for USEPA CLPILM 05.2 (Soil/Sediment)

I. PRINCIPLE

Cyanide from alkaline distillates is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at pH lower than 8. The CNCl then forms a red-blue dye by reacting with pyridine-barbituric acid reagent. The color is read at 570 nm.

II. INTERFERENCES

1. For total cyanide, most interferences are eliminated or minimized by the distillation procedure. Sulfides (sulfides are removed with a lead acetate scrubber using the maxi distillation system) fatty acids, aldehydes and thiocyanates may distill over. See Empirical Laboratories Method SOP-164 for distillation procedure.

III. SPECIAL APPARATUS

1. Lachat Quick Chem AE Automated Ion Analyzer

2. Cyanide manifold (Lachat)

IV SAMPLE HANDLING AND PRESERVATION:

The color reaction is pH sensitive. Therefore, distillates and standards should be carefully matched with respect to NaOH concentration. The distillates are 0.25 N NaOH.

V. SAMPLE PREPARATION

The samples for analysis come directly from the midi-scale distillation procedure.

VI. PREPARATION OF REAGENTS

Use deionized water (<10 megaohm) for all solutions.

Degassing with helium

To prevent bubble formation in the flow cell which can cause inaccurate readings due to airspikes (characterized by poor peak integrity factors (PIF) and/or inaccurate results) degass all solutions except the standards and the Pyridine-Barbituric Acid reagent with helium. Use Helium at 140 kPa (20 lb/in^2) through a helium degassing tube (Lachat part 50100). Bubble Helium vigorously through the solution for one minute.

Reagent 1. Carrier, 0.25 M Sodium Hydroxide

In a 1L vol. flask add 200 mL of 1.25N NaOH (which is used in the SOP-164 distillation method) to approximately 600 mL of D.I. water. Dilute to 1 L, invert to mix. This will ensure that the concentration of the NaOH used for the distillates will be the same concentration used for the carrier solution.

Reagent 2. Phosphate Buffer, 0.71 M

In a 1 L volumetric flask, dissolve 97 g anhydrous potassium dihydrogen phosphate (potassium phosphate, monobasic, anhydrous, KH_2PO_4) in approximately 800 mL water. Dilute to the mark and invert to mix. Prepare fresh monthly.

Reagent 3. Chloramine-T Hydrate

To a 500 mL volumetric flask add about 250 mL water, then add 2.0 g chloramine-T [$CH_3C_6H_4SO_2N(Cl)Na \times H_2O$]. Dilute to the mark and invert to mix. Prepare fresh daily. The shelf life of the chloramine-T can be a critical factor in the Lachat run. New Chloramine-T should be ordered every 6 months. (Analyst discretion should be used).

Reagent 4. Pyridine-Barbituric Acid Reagent

In the fume hood, place 15.0 g barbituric acid in a 1 L beaker and add 100.0 mL water, rinsing down the sides of the beaker to wet the barbituric acid. Add 75 mL pyridine (C_5H_5N) with stirring and mix until the barbituric acid dissolves. Add 15 mL concentrated hydrochloric acid (12 M HCl) and mix. Transfer to a 1 L volumetric flask, dilute to the mark, and invert to mix. This reagent is stable for approximately six months if stored in a cool, dark place.

VII. PREPARATION OF STANDARDS

Traceability

A bound logbook record shall be maintained on all reference materials. The record shall include date of receipt, source, purity, all compositional information, storage conditions and expiration date. These materials/solutions are to be identified by a unique number in the logbook as well as on the container's label.

All working standards made from reference materials shall be labeled with a unique ID number with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date and the logbook where information is recorded. Reagents shall be labeled with date received and expiration date, if applicable. All of the information described above shall also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations, volume diluted to, etc.) shall also be recorded. There should be no container with sample, sample extract, standard solution, etc. that is not correctly labeled and properly stored.

The analyst must initial and date each entry made in a logbook. Each analyst must be sure to "Z" out the unused area of each logbook page.

Standard 1. 1000 mg CN/L [~1,000 mg CN^-/L (Stock)]

The Stock Standard is purchased from a vendor. **CAUTION: KCN is highly toxic. Avoid contact with standard solutions. Use gloves and protective equipment when handling standards and samples.** This solution is given a unique identifier.

NOTE: The cyanide ion present in the original sample is concentrated by the macro-distillation procedure. The standards preparation recipes below are for standards which are not distilled. These standards are prepared in 0.25 M NaOH to match the matrix of the distilled samples. Since the samples are concentrated by a factor of two; a x 0.50 correction factor must be included in the final manual dilution factor entered into the Lachat. For example, a x 100 dilution would have a final manual dilution factor of 50 and an undiluted sample would have a final manual dilution factor of 0.50.

Record preparation in the appropriate log book.

Standard 2. Working Standard (10.0 mg CN/L)

Pipette 2.00 mL Standard 1 into a 200 mL volumetric flask. Dilute to the mark with Reagent 1, 0.25 M Sodium Hydroxide. Invert to mix.

Set of six calibration Standards:

10 mL of 10 mg/L diluted to 100 mL = 1.0 mg/L std
5.0 mL of 10 mg/L diluted to 100 mL = 0.500 mg/L std
2.0 mL of 10 mg/L std diluted to 100 mL = 0.200 mg/L std
1.0 mL of 10 mg/L std diluted to 100 mL = 0.100 mg/L std
4 mL of 0.500 mg/L std diluted to 100 mL = 0.020 mg/L std
2 mL of 0.500 mg/L std diluted to 100 mL = 0.010 mg/L std
1 mL of 0.500 mg/L std diluted to 100 mL = 0.0050 mg/L std
Blank consists of 0.25 M NaOH
10 mL of 10.0 mg/L std diluted to 200 mL = 0.500 mg/L chk std

The diluent for all standards is 0.25 M NaOH.

NOTE: The cyanide standards are labeled by their actual concentration as determined by standardization of the cyanide stock. For example, if the cyanide stock was determined to have a concentration of 994 mg/L (instead of 1,000 mg/L) then the "1.00 mg/L" std would actually be 0.9940 mg/L, the "0.200 mg/L" std would be 0.1988 mg/L, and so forth. Assigning values to the standards is done under the "Method Definition" option on the Lachat computer.

Record preparation in the appropriate log book.

VIII. INSTRUMENT INFORMATION (see page 12 for manifold diagram)

Analyst should confirm the following:

A. Timing:

Sample throughput: 80 samples/h; 40 s/sample
Pump speed: 35 RPM

Cycle Period: 45 s
Inject to start of peak period: 28 s
Inject to end of peak period: 61 s

B. QuikChem AE Settings:

1) Parameter, Data Window:

Top Scale Response: 0.50 abs
Bottom Scale Response: 0.00 abs

2) Segment/Boundaries

A - 0.50 mg CN/L
F - 0 mg CN/L

3) Results/Approval, Reports

In the default Report definition file (RDF), change:
-Set Default Chord 0 to
-Set Default Chord 3
(Peak should be centered in chord 3)
This change must be made to both the sample and the calibration RDF's.

C. System Notes:

1. Allow enough time for heating unit to warm-up to 60°C with D.I. water pumping through all reagent lines at full speed. (approximately 30 min.)

IX. CALCULATIONS

A. Aqueous Samples:

The Lachat reports the concentration of the final distillate in mg/L. To correct for the X2 concentration by the distillation process, a x 0.50 correction factor must be included in the final manual dilution factor when defining a tray in the Lachat computer. For example, a x 100 dilution would have a final manual dilution factor of 50 and an undiluted sample would have a final manual dilution factor of 0.50. After the application of the X0.5 correction factor, the detection limit is 0.005 mg/L.

B. Solid Samples:

The Lachat reports the concentration of the final distillate in mg/L. Results for solid samples should be in mg/kg and can be obtained by entering the appropriate dilution factor when defining the tray. Conversion from mg/L to mg/kg can be accounted for by the following formula:

$$\left[\frac{\text{mg CN}^-}{\text{Kg sample}}\right]=\left(\frac{\text{N mg}}{\text{1 L soln}}\right)\left(\frac{\text{0.50 L soln}}{\text{g sample}}\right)\left(\frac{\text{1,000 g sample}}{\text{1 Kg sample}}\right)(\text{Wet Weight})$$

From this formula a dilution factor can be obtained. For example if 2 grams of soil were used then this would be a x 250 dilution. When the x 0.50 correction factor is included a final manual dilution factor of x 125 is obtained.

N would be the value obtained from the Lachat without a correction factor. The minimum value for N is 0.01 mg/L soln.

C. Data reporting

1. Reduce data to the result which will be reported.

2. Complete the data review checklist (attached). This must be completed and attached to each set of USACE data.

X. QUALITY CONTROL (Reference SW-846, Update III and USEPA CLP ILMO 4.1 for further clarifications)

A. QA/QC, distilled:

1. PB (preparation blank)

500 mL of DI water are distilled. When brought up to 250 mL volume following the distillation process a 0.25 M NaOH solution is obtained. A blank is distilled every batch of samples. If the absolute value of the PBW is not below the CRDL or the RL **or ½ the CRDL for Navy Projects** the analyst's supervisor should be consulted before proceeding.

2. DCV (distilled calibration verification)/ICV (distilled/CLP)

a. The DCV is a check standard generally of a concentration of about 0.200 mg/L. A DCV is put on with every set of distilled samples. There is a maximum of 10 samples in a set. If the DCV is not within ±10 % of the undistilled value the analyst's supervisor should be consulted before proceeding. This sample is given a unique identifier in the distillation log. **USACE projects require both a high and low level DCV and they should compare within ±10% of the undisdilled standards. A corrective action report (CAR) will be required if the limit is exceeded.**

b. CLP requires the ICV to be distilled and from a second source. Must be analyzed immediately after calibration. For water samples the ICV will serve as the LCS (water only). Soils require bath. The control limit is ± 15%.

3. LCSW (laboratory control sample-water)

The laboratory control sample is a second source check on the calibration and must be run once every 20 aqueous samples. The control limits are in-house-generated. The CLP control limits is 80 to 120%. If the LCSW is not within control limits the analyst's supervisor should be consulted before proceeding. This sample is given a unique identifier in the distillation log.

4. LCSS (laboratory control sample-soil)

The LCSS is a second source check with a soil matrix and must be run once every 20 solid phase samples. The control limits are in-house-generated. Under CLP the agency may set the limits. If not, use in-house control limits. If the LCSS is not within control limits the analyst's supervisor should be consulted before proceeding. This sample is given a unique identifier in the distillation log.

5. MS/MSD (matrix spike/matrix spike duplicate)

A spike and spike duplicate (CLP requires 1 duplicate and 1 matrix spike) are done with each batch or 20 samples. The spike concentration will usually be the same as the DCV and spikes are added to the boiling flask in the same manner as check standards. Included in the boiling flask will be the sample aliquot. The total volume for the matrix spike is 500 mL. If the percent recovery for the MS or MSD is not within ±25 percent of the spike concentration, the analyst's supervisor should be consulted before proceeding.

6. Documentation of Capability (DOC) - Each analyst must perform a DOC to demonstrate proficiency with this method. Refer to SOP-413 for guidance.

B. QA/QC, undistilled:

1. ICV (initial calibration verification)

The ICV is an undistilled check standard made from the working standard solution. The concentration is usually around the midpoint of the calibration curve (about 0.500 mg/L). The ICV is analyzed at the beginning of each Lachat run. If the ICV is not within ±10 percent of its true value, the analyst's supervisor should be consulted before proceeding. The calibration verification standard must be prepared fresh daily.

2. ICB (initial calibration blank)

The ICB is 0.25 M NaOH solution and follows the ICV at the beginning of each Lachat run. If the absolute value of the ICB is not IRL or ± CRDL **or ½ the CRDL for Navy Projects**, the analyst's supervisor should be consulted before proceeding.

3. CCV (continuing calibration verification) **From primary std. that curve is made from.**

   The CCV will be analyzed after every 10 samples and at the end of the tray. The sampling of the CCV's will be done automatically by the Lachat if it is included in the tray definition. The CCV scheduling can be done under the Data Quality Management option in the Tray Definition screen. If the CCV is not within ±10 percent of its true value a CHK STD failure signal will be given by the Lachat and the analyst's supervisor should be consulted before proceeding.

4. CCB (continuing calibration blank)

   This sample verifies the instrumental baseline. If the absolute value of the CCB is not below the minimum detection limit the analyst's supervisor should be consulted before proceeding.

C. Calibration Approval:

For a cyanide calibration to be approved, segment (A-F) of the curve must have a correlation of at least 0.995 in chord 3.

D. Method Detection Limit (MDL), Empirical Laboratories Reporting Limit (ERL), Contract Required Quantitation Limit (CRQL) and Analyte Wavelength:
(MDLS are performed annually or whenever a change in the method is made.)

TABLE I

Aqueous and Soil Method Detection Limits(MDL), Empirical Laboratories Reporting Limits(ERL), CLP OLM04.1 & OLM05.2 Contract Required Quantitation Limits (CRQL)

Analytes by EPA 335.1, 335.3, 9012A , SOW 4.1 & 5.2	AQUEOUS MDL(ug/L)	AQUEOUS ERL(ug/L)	AQUEOUS CRQL ILMO 4.1 (ug/L)	AQUEOUS CRQL ILMO 5.2 (ug/L)	SOLID/SOIL MDL (mg/Kg)	SOLID/SOIL ERL (mg/Kg)	SOLID/SOIL CRQL ILMO 4.1 (mg/Kg)	SOLID/SOIL CRQL ILMO 5.2 (mg/Kg)
Cyanide	0.0050	0.005	10	10	0.007	0.13	1	1

TABLE II

ANALYTE WAVELENGTH	
Cyanide	570.0

XI. CORRECTIVE ACTIONS

A. INSTRUMENT RELATED

1. ICV not within ± 10%

   a. If the problem is with the solution.

      i. Reprepare, obtain new stock if necessary.

   b. If the problem is with the calibration.

      i. Recalibrate thru analysis of appropriate standards and recheck ICV.

2. CCV not within ± 10%

   a. If the problem is with the solution.

      i. Reprepare, obtain new stock if necessary.

   b. If the problem is with the calibration.

      i. Recalibrate thru analysis of appropriate standards and reprepare/reanalyze the previous ten sample according the following guidelines.

         a. If the CCV was biased high, any of the previous ten samples which were BMDL do not require reanalysis.

         b. If the CCV was biased low, the previous ten samples must be reanalysed.

3. Ending CCB not ± RL or CRDL **or ½ the CRDL for Navy Projects**
   a. If the CCB is biased high.

      i. Any samples BDL or greater than 5X the CCB bias need not be reanalyzed.
      ii. Any samples above the detection limit but less than 5X the CCB level must be reanalyzed after the problem is corrected.

   b. If the CCB is biased low.

      i. Any samples greater than 5X the absolute CCB bias need not be reanalyzed.
      ii. All other samples must be reanalyzed after the problem is corrected.

B. DIGESTION RELATED

1. The preparation blank is not less than the ± RL or CRDL **or ½ the CRDL for Navy Projects**.

   a. If the problem with the instrument.

      i. Analyze a CCB to determine this.
      ii. If the problem was with the instrument correct the situation and reanalyze the preparation blank.

   b. If the problem is with the distillation.

      i. All associated samples which are BMDL or have a level of cyanide greater than 5X the level found in the preparation blank can be reported. If the level of cyanide in an associated sample is not BMDL nor greater than 5X the level found in the preparation blank, the sample must be redistilled/reanalyzed or reported as qualified. The project manager or QA manager will make this determination.

2. LCS not within our in-house generated control limits (or ±20%).

   a. If the problem is with the instrument.

      i. Reanalyze when instrument is in control.

   b. If the problem is with the digestion.

      i. If biased low, associated samples must be redigested.
      ii. If biased high, the impact upon the data user must be evaluated. The samples will be redigested or the data will be qualified on the final report.

3. Distilled check standard not within control limits of ±15%.

   a. If the problem is with the instrument.

      i. Reanalyze when instrument is in control.

   b. If the problem is with the digestion.

      i. If biased low, associated samples must be redigested.
      ii. If biased high, the impact upon the data user must be evaluated. The samples will be redigested or the data will be qualified on the final report.

C. SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20%

i. The associated sample data must be qualified on the final report.

2. Spike analysis recovery not within ±25%

   i. If the analyte level in the sample is greater than 4X the spiking level, the %recovery can not be evaluated and no action is taken.

   ii. If the analyte level in the sample is not greater than 4X the spiking level, the associated sample data must be qualified on the final report.

XII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIII. SOURCES/REFERENCES:

1. Lachat manual; Quick Chem method 10-204-00-1-A.

2. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983, Method 335.4.

3. Standard Methods for the Examination of Water and Wastewater, 14th Edition, APHA-AWWA-WCPC, Park 413D, pp. 370-372.

4. SW-846, 9012A, Revision September 1986.

5. U.S. Environmental Protection Agency, C.L.P. S.O.W. ILMO 4.1.

6. QuickChem AE, Automated Ion Analyzer Training Manual, Lachat Instruments.

7. QuickChem AE, Automated Ion Analyzer Software Reference Manual, Lachat Instruments.

Addendum for USEPA CLPILM 05.2 AQUEOUS &SOIL/SEDIMENT

The following is a list of changes for sample preparation when the 5.2 statement of work is required:

1. The ICV shall be distilled.

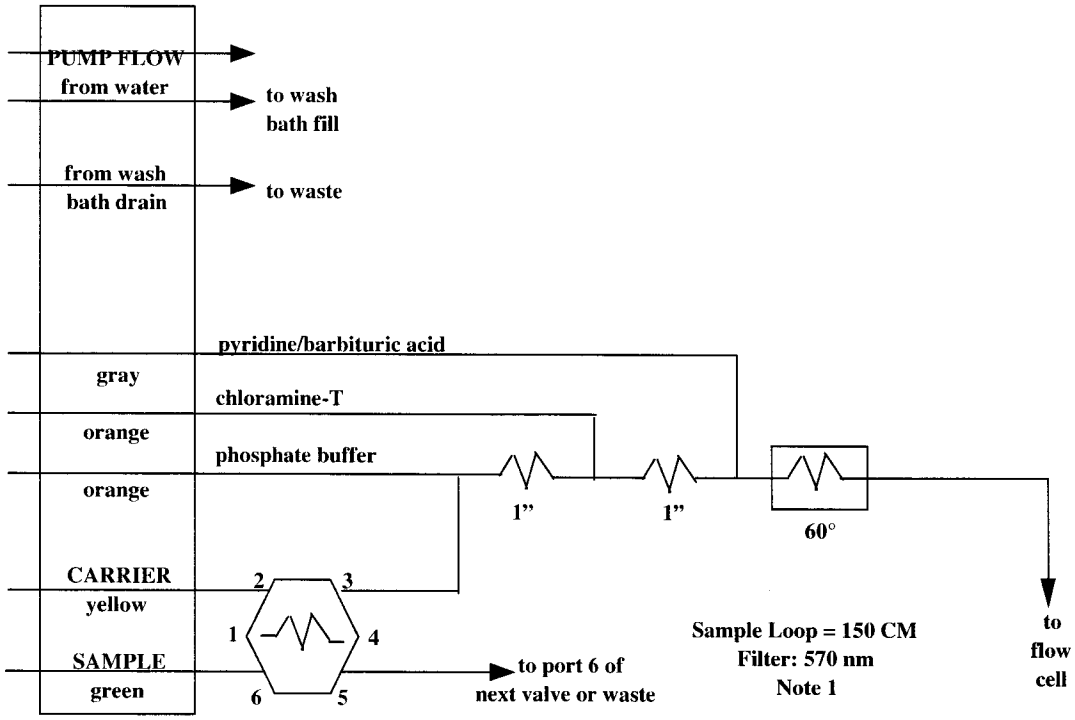
2. Boiling chips are to be added to each sample. Midi-Distillation is reflux 1.5 hours then the heat and vacuum is turned off and the samples cool an additional 15 minutes.

3. The QC criteria for both the Distillation Check QC and the distilled ICV is ±15%.

4. A CRI is required at the beginning and end of each run and for every 20 samples. The QC criteria for the CRI is ±30%.

5. Rounding rule for the appropriate level of precision is that the figure following those to be retained is ≥ 5, round up: otherwise round down. (examples: 1.5 and 2.5 would be 2 and 3 respectively rounded up; 1.4 and 2.4 would be 1 and 2 respectively rounded down) Please see Exhibit B, Section 3, (3.3.9.1) of SOW ILM0 5.2 for more guidance on rounding significant figures.

MANIFOLD DIAGRAM



CARRIER is 0.25 M Sodium Hydroxide

1" is 70.0 cm of tubing on a 1 in coil support

APPARATUS: Standard valve, flow cell, and detector head modules are used. The box shows 650 cm of heated tubing.

All manifold tubing is 0.8 mm (0.032 in) i.d., This is 5.2 µL/cm.

Note1: A 3.0 m x 0.022" id back pressure loop is placed at the exit of the flow cell.

Manifold Diagram Revision Date: 13 May 1992

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):	
Batch Number(s):	
Method:	**9012A (Cyanide)**

QA/QC Item	Yes	No	NA	Second Level Review
1. Were samples analyzed within USACE holding times?				
2. Was initial calibration curve QC criteria met?				
3. Was all continuing calibration criteria in control?				
4. Did any sample exceed the highest calibration standard? (If yes, were appropriate dilutions made to generate samples concentration within calibration range?)				
5. Did LCS or blank spike meet control limits?				
6. Did MS/MSD meet control limits?				
7. Was the preparation (Method) Blank below the project required detection limits?				
8. Did you return samples back to cold storage immediately after use?				
9. Was distillation temperature monitored/documented and did you apply the thermometer correction factor?				
10. Sample preparation information is correct and complete.				
11. Analytical results are correct and complete.				
12. The appropriate SOP's have been used and followed.				
14. "Raw data" including all manual integration's have been correctly interpreted.				
15. "Special" sample preparation and analytical requirements have been met.				
16. Documentation complete (e.g., all anomalies in the analytical sequence have been documented, corrective action forms are complete.				

ANALYST DATA REVIEW CHECKLIST
9012A (Cyanide)

Comments on any "No" response:

_____
_____
_____
_____
_____
_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

Empirical Laboratories, LLC

NITRATE/NITRITE, NITRITE IN SURFACE WATER, WASTEWATER 0.02 TO 2.0 mg N/L and NO_3^- or NO_2^-

USEPA METHOD 353.2, Lachat Method 10-107-04-1-A

SOP NUMBER: SOP-179

REVISION NUMBER: 4

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 11/29/06

DATE OF LAST REVIEW: 11/29/06

Empirical Laboratories, LLC

NITRATE/NITRITE, NITRITE IN SURFACE WATER, WASTEWATER 0.02 to 2.0 mg N/L and NO_3^- or NO_2^- BY EPA METHOD 353.2

I. SCOPE AND APPLICATION

1.1 The purpose of this method is to determine nitrate/nitrite in surface waters, and industrial wastewaters.

1.2 The applicable range is 0.05 to 2.0 mg N/L as NO_3^- or NO_2^-. The statistically determined method detection limit or limit of detection as determined in water is 0.01 mg N/L. The reporting limit is 0.050 mg/L. All samples are diluted five times before analysis. The method throughput is 55 injections per hour.

1.3 Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure from the method section 11.

II. SUMMARY OF METHOD

2.1 Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrchloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Nitrite alone also can be determined by running without the cadmium column.

III. PRINCIPLE

Nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting water soluble dye has a magenta color which is read at 520 nm. Nitrite alone also can be determined by removing the cadmium column.

IV. INTERFERENCES

4.1 Residual chlorine can interfere by oxidizing the cadmium column.

4.2 Low results would be obtained for samples that contain high concentrations of iron, copper or other metals. In this method, EDTA is added to the buffer to reduce this interference.

4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

4.4 Sample turbidity may interfere. Remove turbidity first by filtration with 0.45 µm pore diameter membrane filter prior to analysis.

4.5 Sample pH effects column efficiency. Ensure that all samples have been properly preserved with H_2SO_4 at a concentration proportional to 2 mLs of H_2SO_4 per liter of sample.

V. DEFINITIONS

5.1 ANALYTICAL BATCH-The set of samples extracted /distilled/ or digested at the same time to a maximum of 20 samples.

5.2 CALIBRATION BLANK (CB)- A volume of reagent water in the same matrix as the calibration standards, but without the analyte.

5.3 CALIBRATION STANDARD (CAL)- A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

5.4 FIELD BLANK (FMB)- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all preanalysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

5.5 FIELD DUPLICATE (FD)- Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

5.6 LABORATORY BLANK (LRB)- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to determine if the analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

5.7 LABORATORY CONTROL SAMPLE (LCS)- A solution prepared in the laboratory by dissolving a known amount of one or more pure compounds in a known amount of reagent water. Its purpose is to assure that the results produced by the laboratory remain within the acceptable limits for precision and accuracy. (This should not be confused with a calibrating standard, it must be prepared from a source other than the same source as the calibration standards).

5.8 LABORATORY DUPLICATE (LD)- Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

5.9 QUALITY CONTROL CHECK SAMPLE (QCS)- A sample containing analytes of interest at known concentrations (true value) of analytes. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal preparation process.

5.10 METHOD DETECTION LIMIT (MDL)- The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

VI. EQUIPMENT AND SUPPLIES

6.1 Lachat QuikChem FIA+, 8000 Series

6.2 520 nm interference filter.

6.3 Cadmium-Copper Reduction Column (Lachat Part # 50237). Purchased pre-packed from Lachat.

6.3.1 CADMIUM COLUMN INSERTION PROCEDURE

6.3.1.1 Before inserting the column, pump all reagents into manifold.
6.3.1.2 Turn the pump off.
6.3.1.3 On the column, disconnect the center tubing from one of the union connectors and immediately connect to the outlet tubing of the buffer mixing coil.
6.3.1.4 Connect the open tubing on the column to the tee fitting where the color reagent is added. **DO NOT LET AIR ENTER THE COLUMN.**
6.3.1.5 Return the pump to normal speed.
6.3.1.6 The direction of reagent flow through the column is not relevant.

6.3.2 CADMIUM COLUMN MAINTENANCE

6.3.2.1 To store the column and maximize its life span and efficiency:
Note: At no time allow air to enter the column.

6.3.2.2 Close the column by-pass valve.
6.3.2.3 Place all reagent lines into clean DI H_2O.
6.3.2.4 When all air is out of system, open the column by-pass valve and rinse manifold for 2 to 3 minutes.
6.3.2.5 Close the column by-pass valve.
6.3.2.6 Place all reagent lines in NH_4Cl Buffer solution.
6.3.2.7 When all air bubbles are out of the system, open the column by-pass valve and allow the buffer to fill the column. This takes about 2 to 3 minutes.
6.3.2.8 Close the column by-pass valve.
6.3.2.9 Rinse the manifold with clean DI H_2O for 2 to 3 minutes.
6.3.2.10 Remove all tubing from the DI H_2O and run the pump until the manifold is dry.

VII. SAMPLE HANDLING AND PRESERVATION

7.1 Samples should be collected in hard or soft plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

7.2 Nitrite will be oxidized by air O_2 to nitrate in a few days. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they must be preserved with sulfuric acid (2 mL conc. H_2SO_4 per liter) and refrigerated. The holding time is 28 days.

7.3 Caution: Samples must not be preserved with mercuric chloride or thiosulfate because this will degrade the cadmium column.

7.4 If build-up of suspended matter in the reduction column restricts sample flow, the samples may be pre-filtered.

VIII. PREPARATION OF REAGENTS

8.1 Use deionized water (10 megohm) for all solutions.

8.2 Reagent 1. Acidified Deionized Water
Volumetrically, add 4.0 mL of conc H_2SO_4 to 1500 mL DI H_2O in a 2L volumetric flask. Dilute to mark and mix.

In order to maintain a matrix match between the pH of the standards used to create the calibration curve, the quality control standards, and the client samples, acidified deionized water is utilized as the diluent and blank matrix. When new acidified DI H_2O or NH_4Cl buffer is used, the pH matrix balance maybe shifted. This may cause the initial quality control samples to fail. If this occurs it may be necessary to adjust the pH

of the system to match that of the calibration run. This is accomplished by varying the amount of acid in the carrier solution. A more acidic solution will lower the values read, and raising the pH of the acidified DI H_20 will raise the concentration values.

NOTE: Changing the acidity of the carrier solution should be done only after all other possible sources of trouble have been eliminated (check for leaks and clogs in the tubing, QC standard preparation, proper tension on pump tubing, etc.)

Store in plastic bottles at room temperature.

8.3 Reagent 2. Ammonium Chloride Buffer, pH 8.5

By Volume: In a hood, to a 1 L volumetric flask add 500 mL water, 105 mL concentrated hydrochloric acid (HCl), 95 mL ammonium hydroxide (NH_4OH), and 1.0 g disodium EDTA. Dissolve and dilute to the mark. Invert to mix. Adjust pH to 8.5 with HCl or NH_4OH. **The pH should be checked each time the reagent is used and adjusted back to 8.5.**

NOTE: Reagents 1 and 2 determine the pH of the final product and need to be prepared as consistently as possible from batch to batch to ensure accurate results.

8.4 Reagent 3. Sulfanilamide Color Reagent

By Volume: To a 1 L volumetric flask add about 600 mL water. Then add 100 mL of 85 percent phosphoric acid (H_3PO_4), 40.0 g sulfanilamide, and 1.0 g N-(1-naphthyl)ethylenediamine dihydrochloride (NED). Shake to wet, and stir to dissolve for 30 minutes. Dilute to the mark, and invert to mix. Store in a dark bottle. This solution is stable for two months.

IX. PREPARATION OF STANDARDS

9.1 Following are standards preparations for one channel system determining NO_2^- + NO_3^- or NO_2^-. The use of NO_3^- standards is recommended when running a one channel method for NO_2^- + NO_3^-.

9.2 Standard 1. Stock Nitrate Standard 1,000 mg N/L as NO_3^-

Purchased commercially from Fisher at a concentration of 1000 mg/L.

9.3 **Standard 2. Working Nitrate Standard, 20.00 mg N/L as NO_3^-**

By Volume: In a 250 mL volumetric flask, add 5.0 mL Stock Standard 1 (commercially prepared at 1000 mg/L). Dilute to the mark with acidified water (reagent 1) and invert to mix.

9.4 Set of Nine Working NO_3^- Standards:

2.0 mg N/L: Dilute 25.0 mL of 20mg N/L to 250 mL acidified water
1.6 mg N/L: Dilute 20.0 mL of 20mg N/L to 250 mL acidified water
1.2 mg N/L: Dilute 15.0 mL of 20mg N/L to 250 mL acidified water
0.80 mg N/L: Dilute 10.0 mL of 20mg N/L to 250 mL acidified water
0.40 mg N/L: Dilute 5.0 mL of 20mg N/L to 250 mL acidified water
0.20 mg N/L: Dilute 25.0 mL of 2.0mg N/L to 250 mL acidified water
0.10 mg N/L: Dilute 12.5 mL of 2.0mg N/L to 250 mL acidified water
0.050 mg N/L: Dilute 6.25 mL of 2.0mg N/L to 250 mL acidified water
0.000 mg N/L: Blank acidified de-ionized water

Dilute each to the mark with acidified DI H_2O and invert to mix. The nitrate standards have been successfully preserved and reused. Standards are good for 5 months. More volume of the 1.2 mg/L standard is needed because the 1.2 standard is the preferred check standard for the Lachat calibration.

9.5 Spiking Solution NO_3^- Standard (10 mg N/L):

By volume, add 50 mLs of Working Standard 2 in a 100 mL volumetric flask and dilute to mark with acified DI H_2O. (same source as calibration standards)

9.6 Laboratory Control Sample

Performance evaluation samples that we have analyzed and received the true values for are used for second source verification of the curve. These standards are documented as to source, concentration and expiration date and given a unique identifier in the Inorganic Standard Log A (ISA).

X. CALIBRATION AND STANDARDIZATION:

10.1 Prepare reagents and standards as described in sections 8 and 9 above.
10.2 Set up manifold as shown in section 17 of the Lachat method.
10.3 Input data system parameters as shown in section 17 of the Lachat method.
10.4 Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.
10.5 Place standards in the sampler. Input the information required by the data system.

10.6 Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the peak area for each standard to determine the calibration curve.

10.7 Verify calibration using a midrange calibration standard (1.2 mg/L) (CCV) every ten samples. Compute the percent recovery using the following equation: %R=D/K x100 where R = recovery, D = Determined concentration of analyte in the calibration standard, K = Actual concentration of the analyte in the calibration standard.

10.8 If recovery exceeds ± 10%, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the samples analyzed must be reanalyzed back to the first acceptable CCV.

A new curve must be prepared at the beginning of each analysis run using the standards as described in section 9.4 correlation coefficient of at least 0.997 must be obtained from the curve, and an LCS must be read with each curve to ensure the curve is correct, the LCS should be well within the acceptable range (80-120%). If not, the analysis must stop and the problem found and corrected before analysis begins.

XI. COLUMN EFFICIENCY PROCEDURE

11.1. Visually inspect the column. Check for air bubbles in the column or lines, gaps in the column or any change in the cadmium surface characteristics, (cadmium granules should be dark gray).

11.2 If air bubbles are present in column, connect the column into the manifold, turn the pump on maximum and tap firmly with a screwdriver handle, being careful not to break the column, working up the column until all air is removed. If air cannot be removed, the column should be repacked. Cadmium columns should be stored filled with buffer. If air enters the column, efficiency will decrease.

11.3 Check the flow efficiency by disconnecting the cadmium column from the manifold and reconnecting to a green pump tube. Pump buffer through the packed column and collect in a graduated cylinder. The flow rate with the column connected should be greater than 4.0 mL/min.

11.4 Determine the column efficiency at the beginning of each analysis run by using the **concentration ratio method**:

1. Calibrate with the mid-range NO_2-N or NO_3-N standards
2. Run a known concentration NO_2-N standard
3. Run a matching concentration NO_3-N standard
4. The column efficiency is determined by the equation:

$$\frac{C_{NO_3\text{-}N}}{C_{NO_2\text{-}N}} \times 100 = E$$

$C_{NO_3\text{-}N}$ = concentration of NO_3 standard
$C_{NO_2\text{-}N}$ = concentration of NO_2 standard
E = % efficiency

5. If the efficiency is <90 percent, the column should be repacked

XII. PROCEDURE

12.1 Prepare reagents and standards as described in sections 8 and 9 above.
12.2 Set up manifold as shown in section 17 of the Lachat method.
12.3 Input data system parameters:

12.3.1 DATA SYSTEM PARAMETERS

12.3.1.1 Timing

Sample throughput: 20 samples/h; 40 s/sample
Pump speed: 35
Cycle period: 40 s

12.3.1.2 **Nitrate + Nitrite:**

Inject to start of peak period: 28 s
Inject to end of peak period: 60 s

12.3.1.3 Parameter, Data Window:

Top Scale Response: approximately 0.50 abs
Bottom Scale Response: 0.00 abs

12.3.1.4 **GAIN** = 140 x 1
12.3.1.5 **Carrier and diluent** is acidified deionized water.
12.3.1.6 2" is 135 cm of tubing on a 2 inch coil support
12.3.1.7 Apparatus: Standard valve, flow cell, and detector head modules are used.
12.3.1.8 All manifold tubing is 0.8 mm (0.032 inches) i.d. This is 5.2 uL/cm.
Notes: This is a two state switching valve used to place the cadmium column in-line with the manifold.

12.4 Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.
12.5 Adjust sample to pH between 5 and 9 before analysis with either concentrated HCl or NaOH for preserved samples.

12.6 Place samples in the autosampler. Input the sample identification required by the data system.

XIII. SYSTEM NOTES

13.1 The manifold used in this procedure is **10-107-04-1-A.** It is designed to read NO2-NO3 over a range of 0.05 mg N?/L to 2.0 mg N/L.

13.2 QuikChem AE: The NO_3^- concentration can be determined in an RDF using the equation ($[NO_2^- + NO_3^-]$/column efficiency.

13.3 SERIES 4000/SYSTES IV: The NO_3^- concentration can be determined in a pseudo-channel using the equation ($[NO_2^- + NO_3^-] - [NO_2^-]$/column efficiency.

13.4 SEGMENT BOUNDARIES:
A - 2.0
C - 0.80
H - 0.00

XIV. QUALITY CONTROL

14.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks (LCS), and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

14.2 INITIAL DEMONSTRATION OF PERFORMANCE

14.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of Linear calibration range and analysis of quality control samples) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

14.2.2 Linear Calibration Range (LCR)—The LCR must be determined initially and verified every 6 months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards.

14.2.3 Quality Control Sample (QCS)—When beginning the use of this method, verify the calibration standards and acceptable instrument performance with the preparation and analysis of a QCS. The performance evaluation samples we run on a daily basis are an

example of a QCS. The concentrations should match stated values within ±20%. If not in this range the source of the problem should be identified and corrected before continuing with on-going analysis.

14.2.4 Method Detection Limit (MDL)—MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows: MDL = t x S where t= Student's value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates, t= 2.528 for twenty one replicates]. S= standard deviation of the replicate analyses.
MDLs should be determined annually, when a new operator begins work, or whenever there is a significant change in the background or instrument response.

XV. ASSESSING LABORATORY PERFORMANCE AND ANALYTE RECOVERY AND DATA QUALITY

15.1 A continuing calibration verification (CCV) (Standard 1.2 mg/L) must be run every tenth sample and at the end of the run. Criteria ±10%. If the CCV is not within 10% reanalyze the CCV solution. If the second analysis confirms calibration to be outside the limits, all data analyzed back to the last acceptable CCV must be reanalyzed after the source of the problem is found and resolved.

15.2 The CCV must be followed by a continuing calibration blank (CCB). Criteria <MDL. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing analysis.

15.3 A preparation blank must be analyzed every twenty samples. Criteria < ½ RL.

15.4 A laboratory control sample must be analyzed every twenty samples. Criteria ± 20%

15.5 A matrix spike and matrix spike duplicate must be analyzed with every twenty samples. Criteria ±25% Spikes are set up on a sample after you know the concentration of that sample. It should be low enough or diluted to be low enough so that 1.0 mg/L NO_3-N can be added to the sample and not be over 2.0 mg/L NO_3-N. The spike is usually 2.0 mls of 10.0 mg/L spiking solution + 18 mLs of sample. The true value of the spike is 1.0 mg/L. This is calculated by:

$$\% \text{ Recovery} = \frac{(\text{Sample} + \text{Spike}) - (18/20\,\text{Sample})}{2/20\,\text{Spike Concentration Used}}$$

XVI. CORRECTIVE ACTION

If an LCS or Preparation blank is out of range or if spike recovery is not within 75 to 125 percent, a corrective action form is necessary. A Nonconformance report must be filled out and attached to the data. Consult your supervisor for specific action.

16.1 INSTRUMENT RELATED

16.1.1. ICV not within ± 10%
- 16.1.1.1. If the problem is with the solution.
  - 16.1.1.1.1 Re-prepare, obtain new stock if necessary.
- 16.1.1.2 If the problem is with the calibration.
  - 16.1.1.2.1 Recalibrate thru analysis of appropriate standards and recheck ICV.

16.1.2 CCV not within ± 10%
- 16.1.2.1 If the problem is with the solution.
  - 16.1.2.1.1 Re-prepare, obtain new stock if necessary.
- 16.1.2.2 If the problem is with the calibration.
  - 16.1.2.2.1 Recalibrate thru analysis of appropriate standards and re-prepare/reanalyze the previous ten sample according the following guidelines.

16.1.3 If the CCV was biased high, any of the previous ten samples which were below the MDL do not require reanalysis.

16.1.4 If the CCV was biased low, the previous ten samples must be re-analyzed.

16.1.5 CCB not >± MDL (USACE)(**For DOD QSM Ver. 3 no analyte detected > 2xMDL, frequency- beginning and ending a run and every 10 samples**)or ± RL.
- 16.1.5.1 If the CCB is biased high.
  - 16.1.5.1.1 Any samples below the MDL or greater than 10X the CCB bias need not be reanalyzed.
  - 16.1.5.1.2 Any samples above the detection limit but less than 10X the CCB level must be reanalyzed after the problem is corrected.
- 16.1.5.2 If the CCB is biased low.
  - 16.1.5.2.1 Any samples greater than 10X the absolute CCB bias need not be reanalyzed.
  - 16.1.5.2.2 All other samples must be reanalyzed after the problem is corrected.

16.1.6 LCS not within our in-house generated control limits (or ±20%).
- 16.1.6.1 If the problem is with the instrument.
  - 16.1.6.1.1 Reanalyze when instrument is in control.
  - 16.1.6.1.2 If biased high, the impact upon the data user must be evaluated. The samples will be re-extracted or the data will be qualified on the final report.

16.2 SAMPLE MATRIX RELATED

16.2.1 Replicate analysis RPD not within ±20%

16.2.1.1 The associated sample data must be qualified on the final report.

16.2.2 Spike analysis recovery not within ±25%

16.2.2.1 If the analyte level in the sample is greater than 4X the spiking level, the %recovery can not be evaluated and no action is taken.

16.2.2.2 If the analyte level in the sample is not greater than 4X the spiking level, the associated sample data must be qualified on the final report.

XVII. DATA ANALYSIS AND CALCULATIONS

17.1 Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting peak area versus standard concentration. Sample concentrations calculated from the regression equation.

17.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard must be diluted and reanalyzed.

17.3 Report sample results for nitrate/nitrite in mg N/L as NO_3^- + NO_2^- to two significant figures for samples above the MDL. Report results below the MDL as less than the detection limit.

XVIII. HEALTH AND SAFETY

18.1 Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of gloves and lab coats is highly recommended.

18.2 Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples which need special consideration have applicable notes on the sample logs.

18.3 MSDS sheets are available for all reagents and standards which have been purchased. These are located on the bookshelf outside the office supply storage room.

XIX. POLLUTION PREVENTION

19.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

19.2. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

19.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

XX. WASTE MANAGEMENT

20.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel," available from the American Chemical Society at the address listed in Section 14.3 from method 300.1.

XXI. METHOD PERFORMANCE

21.1 The method support data are presented in section 17 of the Lachat method 10-107-04-1-A. This data was generated according to a Lachat Work Instruction during development of the method.

21.2 Although Lachat Instrument publishes method performance data, including MDL, precision, accuracy and carryover studies, we cannot guarantee that each laboratory will be capable of meeting such performance. Individual laboratory and instrument conditions, as well as laboratory technique, play a major role in determining method performance. The support data serves as a guide of the potential method performance. Some labs may not be able to reach this level of performance for various reasons, while other labs may exceed it.

XXII. REFERENCES

1. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983, Method 353.2

2. Lachat Instruments, QuikChem Method 10-107-04-1-C, "Determination of Nitrate/Nitrite in Surface and Wastewaters by Flow Injection Analysis", Revised August 2000.

3. Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. Book 5. Chapter A1. U.S. Department of the Interior, U.S. Geological Survey.

Empirical Laboratories, LLC

FILTERABLE RESIDUE
TOTAL DISSOLVED SOLIDS AND
TOTAL DISSOLVED VOLATILE SOLIDS

METHOD 160.1
(GRAVIMETRIC, DRIED AT 180°C)

SOP NUMBER: SOP-186

REVISION NUMBER: 2

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 01/04/02

DATE OF LAST REVIEW: 02/08/06

FILTERABLE RESIDUE
TOTAL DISSOLVED SOLIDS AND TOTAL DISSOLVED VOLATILE SOLIDS
BY EPA METHOD 160.1 (Gravimetric, dried at 180°C)

I. SCOPE AND APPLICATION:

A. This method is applicable to drinking, surface and saline waters, domestic and industrial wastes.

B. The practical range of the determination is 20 mg/L to 20,000 mg/L.

II. METHOD SUMMARY:

A. A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.

B. If residue, non-filterable (TSS) is being determined, the filtrate from that method may be used for residue, filterable.

III. SAMPLE HANDLING & PRESERVATION:

A. Refrigeration to 4°C, to minimize microbiological decomposition of solids.

B. The holding time for solids is 7 days, analysis should begin within 2 days of receipt because of problems in the past with meeting holding times and/or problems with the test that make reanalysis necessary.

IV. DEFINITIONS:

Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to a constant weight at 180°C.

V. INTERFERENCES:

A. Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.

B. Samples containing high concentrations of bicarbonate will require careful and possible prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.

C. Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

VI. EQUIPMENT/APPARATUS:

A. Glass fiber filter discs, without organic binder Whatman 934-AH or equivalent.

B. Filter holder or Gooch crucible adapter.

C. Filtering flask, 500 mL or more.

D. Gooch crucibles, porcelain made by Coors.

E. 100 to 150 mL porcelain crucibles, low wide-form.

F. Drying oven, 70°C ± 2°C.

G. Drying oven, 180°C ± 2°C.

H. Desiccator

I. Analytical balance, capable of weighing to 0.1 mg.

J. Vacuum pump, see note on maintenance this procedure.

VII. CALIBRATION:

The detection limit for TDS is 20 mg/L. (An MDL study must be performed anually to establish this.)

A. Calibrate analytical balance daily or as used by weighing a 50 gram and a 80 gram weight to check calibration. Record weight results.

B. Calibrate analytical balance monthly by checking the whole range of weights in reference standards set.

VIII. PROCEDURE:

A. Crucible Prep:

1. Wash 100 to 150 mL crucibles in hot soapy water, rinse with tap water and then thoroughly inside and out with D. I. water, place in

180°C oven until needed. Make sure that desiccant in desiccator is placed in 105°C oven overnight to dry when the dessicant under-goes a color change.

2. On the day TDSs are to be analyzed, place crucibles in desiccator for 1 hour then get a tare weight and record. After weighing, handle crucible with tongs only.

3. Place a 9.0 CM, 11.0 CM or 12.5 CM 935-AH glass fiber filter, wrinkled surface up, in a clean buchner-funnel (depending on size buchner funnel available). Place buchner funnel in a filtering flask and apply vacuum, wash the filter with three successive 50 mL volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through, discard washings. This rinses the filter and also allows filter to be well seated in the buchner funnel before sample is filtered.

B. Determination of sample volume:

1. The following criteria is used to determine the volume of sample to be used for analysis:

   According to NEW JERSEY CERTIFICATIONS the difference in the weight of the crucible versus the weight of sample in mg cannot be greater than 300 mg. When the difference is 200 mg or more a smaller volume of sample must be used for analysis. Therefore, on all samples which require TDS, when no prior knowledge of the sample is available the conductivity of the sample must be checked and the volume used for analysis adjusted as follows:

CONDUCTIVITY (µmho/cm)	TDS VOLUME (mL)
0 to 2750	100
2750 to 5500	50
5500 to 11000	25
11000 to 27000	10
27000 to 55000	5
55000 to 270000	1

If the conductivity is over 270000 please inform your supervisor.

C. Total Filterable Solids:

1. Place buchner funnel in a clean, dry filtering flask, begin suction. Shake sample vigorously so that a representative sample may be poured off. Rapidly pour 100 mL of sample by means of a 100 mL graduated cylinder onto prepared filter.

2. Filter the sample through the glass fiber filter, rinse three times with distilled water and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

3. Transfer entire volume of filtrate in filtering flask to a weighed crucible and evaporate to dryness in a 70°C ±2 oven. This normally requires 24 hours, or overnight.

4. Dry the evaporated sample for at least one hour at 180°C ±2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 1.0 mg.

D. Total Residual Filterable Volatile Solids (TDVS):

After total filterable solids are run, place crucible used for this purpose in 550 ±50°C furnace for 15 minutes. Allow crucible to cool in desiccator for 1 hour and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 1.0 mg.

IX. CALCULATIONS:

A. Calculate filterable residue as follows:

$$\text{TDS mg/L} = \frac{(A-B)\,1000}{\left(\frac{C}{1000}\right)}$$

Where: A = weight of dried residue + dish in grams
B = weight of dish in grams
C = volume of sample used in mL.

B. Calculate filterable volatile residue as follows:

$$\text{TDVS mg/L} = \frac{(A-B)1000}{\frac{C}{1000}}$$

Where: A = weight of dried residue + dish in grams.
B = weight of dried residue at 550°C ±50°C + Dish I
C = volume of sample used in mL.

X. QUALITY CONTROL:

A. Do a duplicate every tenth sample.

B. Do a total dissolved solids LCS at least once a week to check accuracy of analytical balance and drying ovens. If the first weighing result is within specification limits more weighings are not necessary.

NOTE: Regular maintenance must be done on the vacuum pump periodically. Always check oil holders to make sure oil is in it up to the red fill line before using. Make sure that reservoir is hooked up in line in case water filters over. This reservoir should be hooked up such that any water coming over will be collected in a flask so it will not go directly into the pump itself. This reservoir should be dumped and cleaned out periodically.

XI. MDL DETERMINATION:

A. Refer to SOP 414.

GC/MS DATA AND REPORT CHECK

SOP NUMBER: SOP-200

REVISION NUMBER: 9

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: 8/03/05

DATE OF LAST REVIEW: 8/03/05

GC/MS DATA AND REPORT CHECK

I. SUMMARY

The following describes the process through which data and reports are checked after being quantitated by the TargetDB Windows NT data system.

A. Data Format

The TargetDB Windows NT data system generates a report which contains the following:

1. Quantitation Report - This includes sample identification, date and time analyzed, instrument identification, file information and compound information (compound name, retention time, scan number, quantitation ion, area counts, calculated concentration based on the calibration curve and final concentration based on sample factors).

2. Total Ion Chromatogram - A graphic representation of the GC analysis.

3. Target Analyte Spectrum - Includes (for each analyte) the standard reference spectrum (generated from the instrument on which the analysis was performed or from the NBS library), the subtracted spectrum from the analysis, the unsubtracted spectrum from the analysis and the integrated signals.

B. Primary Analyst Check

The primary analyst is responsible for checking that the sample meets all the appropiate method criteria and confirming the identification of all analytes. If criteria are not met, a NCR, Non-Conformance Report, is generated within 24 hours and forwarded to the organic manager. The data check list is completed.

1. Internal standards: area counts should be within 50 to 200 percent of the daily calibration and retention times should be within 30 seconds of the daily calibration.

2. Surrogates: Percent recoveries must meet in-house limits for the analysis type and matrix. In-house limits are generated annually from a minimum of 20 LCS and method blank data points. A NCR must be generated if the recoveries are outside the in-house limits. The sample must be flagged if the recoveries are outside these limits (unless the sample is NPDES which has no designated surrogate recovery criteria).

3. Target analyte identification is checked against a standard reference spectrum obtained from the instrument on which the analysis was performed or from the NBS library. Basic criteria is the presence of 3 major ions in the proper ratio (except for compounds which do not have 3 major ions). The experience of the operator is invaluable in this identification process.

4. Target analyte quantitation is checked to make sure the proper units have been calculated and all the factors used are correct.

5. Supporting documentation will be supplied in the case of any analyte identification which is questionable or for any other reason the operator deems necessary. The experience of the operator is invaluable in this process.

6. After checking the data, each quantitation report is initialed and dated.

7. The report is sent forward for second check with all data and completed data checklist.

C. Secondary Analyst Check

The secondary analyst is responsible for checking the primary analyst on target identification and quantitation. All target analyte identifications and calculations must be verified using the criteria given above and the quantitation report initialed/dated. The report is then sent forward with all necessary data and data checklist for report generation. A case narrative is generated if requested by the client.

D. Report Generation

The Organic Report Specialist confirms data is organized and a report is generated with the appropriate client list and all required client QC. All calculations from the quant report to the summary report are checked. Also, all report information is checked, including the client information, units, sampling and receiving dates, sample identification and the presence of all necessary target analytes. The summary report is initialed and dated at this time then forwarded to the appropriate Project Manager. The Project Manager checks the report for completeness and forwards it to the administrative assistant.

E. Administrative Assistant

The administrative assistant is responsible for printing the final report on letterhead. After this step, it is given back to the Project Manager.

F. Project Manager Check

The Project Manager, PM checks the report to make sure it is in the format required for the client. The analyte list and the QC are also checked. The report is evaluated for conflicting and/or unusual results. Items which seem questionable are checked against the data and/or discussed with the analyst. The report is then forwarded to the division director to be evaluated and signed. The report is returned to the PM who mails out the final report and generates the invoice.

GC/MS SEMIVOLATILES BY EPA METHOD 625 AND SW846 METHOD 8270C INCLUDING ADDITIONAL APPENDIX IX COMPOUNDS

SOP NUMBER: SOP-201

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APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

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GC/MS SEMIVOLATILES

BY EPA METHOD 625 AND SW846 METHOD 8270C

1.0 SCOPE AND APPLICATION

Please see Appendix for definitions.
This SOP (based primarily on SW-846 Method 8000B/8270C) is used for the analysis of semi-volatile organic compounds in a variety of matrices (soils, sediments, waters, etc.). Methods *Federal Register* Method 625 and CLP Method for Semi-volatiles have also been used in the development of this SOP. The analyses by these various methods are clearly defined in the respective regulatory manuals. A good understanding of these different methods is essential to the performance of each method. A laboratory list of 625 and 8270 analytes with example limits is found attached in the appendix. Other compounds may be analyzed by this SOP as detailed in section 1.0 of SW-846 Method 8270C. Any questions left by this SOP should be answered by reading the methods, paying close attention to SW-846 8000B/8270C, EPA 625 and CLP. If questions still remain unanswered, check with the Organic Lab Manager, QA/QC Officer and/or Technical Director.

2.0 METHOD SUMMARY

After sample preparation using the appropriate extraction technique, the sample is introduced into the GC/MS using direct injection. The analytes are separated in the gas chromatograph by a combination of the temperature program, the pressure program and the capillary column. The analytes are then detected by the mass spectrometer. Analytes are identified by comparing the mass spectra of known standards with the mass spectra from the sample. Analytes are quantitated relative to known standards using the internal standard method.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Section 7.0 and tables 6-1 and 6-2 of the Empirical Laboratories' Quality Assurance Manual include details concerning sample preservation, containers and handling of semi-volatile samples and extracts. All water and non-quarantined soil samples are stored in the walk-in cooler in the sample storage room at a temperature of 4°C. Quarantined soil samples are stored in the large black refrigerator in the sample receiving/log-in room at a temperature of 4°C. All extracts are stored in the Hobart in the Extraction lab at a temperature of 4°C. Water samples have a holding time of 7 days from date of sampling. Soil samples have a holding time of 14 days from date of sampling (unless otherwise specified for the project).

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

4.1 All raw data (samples & QC) must be evaluated for interferences. If contamination occurs, determine whether the source of interference is in the preparation or clean-up of the samples and take corrective action to eliminate the problem.

4.2 Contamination by carryover can occur when samples of high-concentration and low-concentration are analyzed sequentially. To reduce carryover, the sample syringe must

be rinsed with solvent between injections. If an unusually high sample is detected, a solvent blank should be analyzed for cross contamination.

5.0. EQUIPMENT AND APPARATUS

5.1 HP 5890/6890GC complete with electronic pressure control and temperature programmable gas chromatograph suitable for splitless injection.

5.2 Column: RTX-5MS (or equivalent) 30 m x 0.25 mm I.D. x 0.25 µm film thickness fused silica capillary column or RTX-5 SIL-MS 30 m x 0.28 mm I.D. x 0.5µm film thickness.

5.3 HP 5971/5972/5973 mass spectrometer capable of scanning from 35 to 500 amu every second or less, using 70 volts electron energy in electron impact ionization mode. The mass spectrometer is capable of producing a mass spectrum for decafluorotriphenylphosphine, DFTPP, which meets all the tuning criteria of the EPA methods.

5.4 HP 7673A autosampler capable of reproducibility from one injection to another proven by meeting QC and calibration criteria.

5.5 HP GC/MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria.

5.6 Acquisition Software: HP Chemstation system is interfaced to the GC/MS. The system acquires and stores data throughout the chromatographic programs.

5.7 Data Processing Software: Target DB on Windows NT server data system is interfaced to the HP Chemstation. The system accepts and stores acquired data. It plots by extracted ion current profile (EICP). The system is also capable of integrating the abundances in any EICP between specified time or scan-number limits. The most recent NBS mass spectral library is installed.

6.0 REAGENTS

6.1 Methylene chloride **(Please read SOP-336 before handling this solvent in our laboratory.)** – Trace analysis grade.

6.2 Stock standards are purchased in mixtures from reputable vendors. The date they are received is noted on the label and recorded in the BNA standards log book. The date they are opened is noted on the label and recorded in the BNA standards log book along with their lot number and vendor. Each standard that is prepared is recorded in the BNA standards log book and given a sequential number. Each standards label is completed with the standard number, name, preparation date, expiration date, solvent and analyst initials. All stocks and standards are stored in the freezer at a temperature of -15°C ± 5°C from the date they are received/prepared. Standards are brought to room temperature before being used to make standards. Sonication is used if precipitation is observed after bringing to room temperature. The refrigerator and freezer temperature is monitored daily with an annually calibrated thermometer and recorded with calibration correction in the Extraction temperature/calibration logbook.

Makeup of common standards is detailed below. See the BNA standards log book for makeup of other standards.

6.2.1 The Decafluorotriphenylphosphine (DFTPP) tuning standard is prepared as follows (includes benzidine, pentachlorophenol and 4,4'-DDT): Using a 100µL syringe, 100µL (GCM-150, Ultra Scientific @ 1000µg/mL, or equivalent) is injected into a 2.0mL volumetric flask containing approximately 1.2mL methylene chloride (Trace Grade) and diluted to volume with same making a 50µg/mL standard. After capping and inverting several times, the solution is transferred into 2 labeled 2ml, teflon-lined, screw-capped vials and stored in the freezer at -15°C ± 5°C for up to 6 months. A direct injection of 1.0µL is used to tune the instrument.

6.2.2 Calibration standards are prepared from a 200µg/mL working standard at a minimum of five concentrations. Calibration standards are prepared semi-annually unless the initial calibration verification standard indicates a problem. To makeup the 200µg/mL working standard inject the indicated amount of the following standards (or equivalent) into a 10mL volumetric containing approximately 5mL methylene chloride (Trace Grade) and dilute to volume with the same. After capping and inverting several times, the solution is transferred into an appropriate labeled vial, teflon-lined, screw-capped vial and stored in the freezer at -15°C ± 5°C for up to 6 months. See the Appendix for analytes contained in these mixes.

Standard (Interm.A in 10mls)	Conc (µg/mL)	Amount(µL)	Final (ug/mL)
Base/Neutrals Mix 1 (Vendor,Lot#)	2000	1000	200
Benzidines Mix 2 (Vendor,Lot#)	2000	1000	200
Acids Mix (Vendor,Lot#)	2000	1000	200
SV Mix w/ Pyridine & Carbazole (Vendor,Lot#)	2000	1000	200
BN Surrogate (Vendor,Lot#)	5000	400	200
Acid Surrogate (Vendor,Lot#)	10,000	400	400
Catechol (Standard#)	10,000	200	200
Biphenyl (Standard#)	10,000	200	200
Caprolactum (Standard#)	10,000	200	200
Acetophenone (Standard#)	10,000	200	200
Standard (Interm.B in 5mls)	**Conc (µg/mL)**	**Amount(µL)**	**Final (ug/mL)**
Benzidine (Mix # 2)	2000	500	200
Standard (Interm.C in 5mls)			
Atrazine (Standard#)	10,310	97	200
Benzaldehyde (Standard#)	10,590	94	200

Additional Appendix IX compounds can be added using 3 additional mixes, AppIX A,B,C. Refer to standards log.

To makeup the calibration standards, using a 1ml syringe add the appropriate amount of methylene chloride (trace grade) to a 2ml vial. Add the indicated amount of each intermediate standard to the vial. Add 20ul of internal standard to each screw-capped vial and stored in the freezer at -15°C ± 5°C for up to 6 months.

IntmA,Bor C	Amt. of 200ppm std	Amount of 2000ppm Internal Std
2 µg/mL	10 µL	20 µL
5 µg/mL	25 µL	20 µL
10 µg/mL	50 µL	20 µL

20 µg/mL	100 µL	20 µL
30 µg/mL	150 µL	20 µL
40 µg/mL	200 µL	20 µL
50 µg/mL	250 µL	20 µL
60 µg/mL	300 µL	20 µL
70 µg/mL	350 µL	20 µL
80 µg/mL	400 µL	20 µL
90 µg/mL	450 µL	20 µL
100 µg/mL	500 µL	20 µL

The makeup of the 50µg/mL CCV standard is detailed below. Occasionally, unusual compounds are added to the mix so it is best to check the BNA standards log book for exact standard makeup. Note: MS list spikes and full list spikes for LCS and/or MS/MSD are prepared from an alternate source or lot number other than the calibration standards.

50µg/mL CCV standard preparation:

SV3640

using 1ml syringe add the appropriate amount of methylene chloride to a
2ml vial. Add the indicated amount of intermediate / stock standard to the vial.
Add 20ul of internal standard to the vial (**SV 3635**).Soultion stored in freezer at -15deg C+/-5degC for upto 1 week.

50 ug/mL CCV

	Stock Standard	Concentration		50 ug/mL	
SV3515	BNA intermediate mix	200 PPM		250 uL	
SV3517	Benzidine Int.	200 PPM		250 uL	
SV3516	Atrazine benzaldehyde Int.	200 PPM		250 uL	

6.2.3 The Initial Calibration Verification (ICV) standard is prepared from a vendor stock standard at a concentration of 200µg/mL as detailed below.

50µg/mL ICV standard preparation:

(SV2100) ~ 50ug/ml ICV

Into a 1 mL volumetric flask containing Methylene Chloride ~ about 0.6ml, add 250uls of **SV1995 (readystock 200ppm)** and dilute to volume.

Top off w/20uls of Internal Standard **(SV2079)**
Prep'd: 01/08/03 Exp: 03/16/03

(SV2396) ~ 50ug/ml ICV (benzaldehyde & atrazine)

Into a 1 mL volumetric flask containing Methylene Chloride ~ about 0.6ml, add 250uls of **SV2305 (intermediate stock 200ppm)** and dilute to volume.
Top off w/20uls of Internal Standard **(SV2393)**

Prep'd: 09/18/03 Exp: 03/18/04

7.0 PROCEDURE

Prior to using Federal Register 625, SW-846 8270C, or CLP (semivolatile method) the samples are prepared for chromatography using the appropriate sample preparation and

clean up methods (generally SW-846 methods 3510, 3520, 3540, 3550, 3580, EPA method 625 or CLP).

7.1 Chromatographic conditions: Refer to corresponding instrument maintenance log for current gas chromatograph and mass spectrometer conditions.

7.2 Tuning - Prior to any calibration or analysis, DFTPP tuning criteria must be met for a 1.0µL injection of the tuning standard [see below]. Tune must be met every 12 hours sample analysis is to be performed (every 24 hours for *Federal Register* Method 625 except for South Carolina which only allows 12 hours). The injection port performance compounds (pentachlorophenol, benzidine and 4,4'-DDT) are also injected to verify the performance of the injection port and must meet the following criteria. Degradation of DDT to DDE and DDE must not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. For NPDES samples, the benzidine (base/neutral) tailing factor must not exceed 3.0 while the pentachlorophenol (acid) tailing factor cannot exceed 5.0. The calculation for tailing factors is best illustrated in Figure 13 of the *Federal Register* Method 625 which has been placed in the appendix. If degradation is excessive and/or poor chromatography is seen, the injection port may require cleaning and maintenance. It may also be necessary to break off 15-30cm of the capillary column. The mass spectrum of DFTPP is acquired as follows: by using one scan at the apex peak, or by by using the mean of the apex and the preceding and following scans or mean of a symmetric pattern of scans about the apex, or using the average across the entire peak. Background subtraction is accomplished using a single scan or more than 20 scans prior to the elution of DFTPP.

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present, but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

7.3 Calibration

7.3.1 Initial Calibration - An initial calibration curve at no less than five concentration levels must be analyzed (only three concentration levels are required for *Federal Register* Method 625) and shown to meet the initial calibration criteria before any sample analysis may be performed. Method 625

requires that the %RSD be less than 35% to use the average response factor for quantitation, the curve is to be used otherwise and should have a correlation coefficient (*r*) of ≥0.995 linear, 0.99 and six points for quadratic. Method 8270C requires that the %RSD be less than 15% to use the average response factor for quantitation, the curve is to be used otherwise as long as *r* is ≥0.995 linear, 0.99 and six points for quadratic. In addition, there are calibration check compounds (CCCs) which must have a %RSD less than 30% and system performance check compounds (SPCCs) which must meet a minimum avarage response factor of 0.050. The lowest standard must be less than or equal to the reported quantitation limit and the highest standard must not exceed the linear range of the detector. Generally, levels for the curve are 2 ug/mL, 5 µg/mL, 10 µg/mL, 20 µg/mL, 30 µg/mL, 40 µg/mL, 50 µg/mL, 60 µg/mL, 70 µg/mL, 80 µg/mL, 90 ug/mL and 100 µg/mL. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram. Refer to SOP-224 for guidance. All integrations are checked for acceptability. Response factors of less than 0.050 must be supported by the mass spectrum of the lowest standard. Retention times are set using the midpoint of the curve.

CCCs:	Base/Neutral	Acid
	Acenapthene	4-Chloro-3-methylphenol
	1,4-Dichlorobenzene	2,4-Dichlorophenol
	Hexachlorobutadiene	2-Nitrophenol
	N-Nitroso-di-phenylamine	Phenol
	Di-n-octyl-phthalate	Pentachlorophenol
	Fluoranthene	2,4,6-Trichlorophenol
	Benzo(a)pyrene	

SPCCs:	Base/Neutral	Acid
	N-Nitroso-di-n-propylamine	2,4-Dinitrophenol
	Hexachlorocyclopentadiene	4-Nitrophenol

7.3.2 Initial Calibration Verification (ICV) - A second source standard at the 50 µg/mL level is used to check the validity of the curve. The standard recovery for all analytes must be between 75 and 125%. If the second source recovery is above 125%, it is possible that the main standard has deteriorated for that compound. That standard should be remade and reevaluated. If that does not correct the problem, the standard should probably be replaced and a new curve generated. If the second source recovery is below 75%, the second source standard may have deteriorated for that compound. The standard should be remade and reanalyzed. If this does not correct the problem, the standard should probably be replaced. If any compound in the ICV exceeds the criteria above, it may be evaluated and initialed by the organic section manager. If deemed acceptable, the analyst may continue analysis. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram. All integrations are checked for acceptability. For ICV standard preparation refer to standard log book.

7.4 Continuing Calibration Verification (CCV)- Every 12 hours a CCV at 50 µg/mL must be analyzed and calculated against the initial calibration curve, then shown to

meet the calibration check criteria before any sample analysis may be performed. Acceptance criteria for 8270C consists of the same SPCC requirements as the initial calibration. The CCCs must be less than or equal to 20% difference or drift (%D, calculations follow in section 7.9). If any of the CCCs do not meet the above limits, then all required analytes must be <20%D. Internal standard areas should be within 50 to 200 percent of the area of the curve midpoint or the previous CCV. Retention times for the internal standards should be within 30 seconds of the retention time of the curve midpoint or the previous CCV. Method 625 requires a %D of less than 20% for all required analytes. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram. All integrations are checked for acceptability. Samples are then quantitated against the initial calibration curve. Note: If any compound in the continuing calibration not subject to the criteria above exceeds 30%D, it must be evaluated and initialed by the organic section manager. If deemed acceptable, the analyst may continue analysis.

7.5 LCS - The LCS is extracted 1 per extraction batch of up to 20 samples. The LCS containing all regular calibrated compounds is spiked into deionized water using an alternate source or lot number than the calibration standards. See the LCS report forms in the appendix for example laboratory generated limits and the NPDES limits for 625 samples. Recoveries for the MS/MSD spike analytes in LCSs are charted annually to generate control limits for samples analyzed by method 8270C. In all cases, the lowest upper limit would be 100% and the lowest lower limit would be 10%. If enough data points are not present to generate limits, the limits default to CLP spike limits for spike analytes or 10-100% for all other analytes. See Section 8.3 below for corrective action.
When analyzing samples for DOD QSM Version 3, DOD limits will be used.

7.6 Method Blank - Method blanks are extracted at a minimum of 1 per extraction batch up to 20 samples. See Section 8.4 below for criteria and corrective action.

7.7 Samples - Prior to analysis, 1.0 mL samples are prepared by verifying volume and spiking with 20uL of the internal standard solution.

7.8 Instrument sequence-The instrument sequence log is filled out prior to sample analyses.

An example of a typical instrument sequence log follows:
1-DFTPP Tune (12:00 am)
2-CCV
3-LCS
4-Method Blank (or sample)
5-Sample
6-Sample
7-Sample
8-Sample
9-Sample

10-Sample
11-Sample-MS
12-Sample-MSD
13-Sample
14-Sample
15-Sample
16-DFTPP (12:00pm - 12 hours since last DFTPP/CCV)
17-CCV
18-Sample
19-Sample
20-Sample

7.9 Data Reduction/Evaluation - Each sample analysis sequence is documented using the computer run log generated on the chemstation. This run log is signed, dated and paginated then placed in a 3 ring binder for that instrument. After the sample has been analyzed, the data is processed through Target DB on the Windows NT data system. The following must be checked to determine if the sample will need any reanalysis or dilution. Formal data evaluation is detailed in SOP-200 and documented using the Analyst Data Review Checklist (see Appendix).

7.9.1 Internal Standards - Areas should be within 50 to 200 percent of the area of the curve midpoint. Retention time should be within 30 seconds of the retention time of the curve midpoint. If not, the sample and historical data should be evaluated to determine the cause of the problem. If matrix effect is confirmed by reextraction/reanalysis or historical data, complete a corrective action report and flag the affected compounds on the final report for matrix effect. Note: criteria applies to the continuing calibration, not samples, but is used as an indication of the sample analysis validity.

7.9.2 Surrogates – Control limits are determined annually by charting LCSs and method blanks. In all cases, the lowest upper limit would be 100% and the lowest lower limit would be 10%. All of the three surrogates for each fraction must be within the control limits in order for the extraction batch to be in control. If a surrogate exceeds the limits, the reason for the malfunction must be determined and a corrective action report must be completed. The sample must be reanalyzed, reextracted or flagged for QC problems. *Federal Register* Method 625 contains no criteria for surrogate recovery. **When analyzing samples for DOD QSM Version 3, DOD limits will be used.**

Surrogate	Water	Soil/Sediment
Nitrobenzene-d5	35-110	30-110
2-Fluorobiphenyl	30-110	35-110
Terphenyl-d14	55-115	55-110
Phenol-d6	15-110	30-110
2-Fluorophenol	20-110	30-110
2,4,6-Tribromophenol	45-115	45-110

7.9.3 Analyte concentration must be within the range of the calibration curve after rounding to 2 significant figures. If an analyte exceeds the curve, a dilution

must be performed and the next sample must be checked for carryover. Any dilution should keep the concentration of the analyte in question within the top half of the curve.

7.9.4 The qualitative identification of compounds is based on retention time and a comparison of the sample mass spectrum, after background subtraction, with characteristic ions in a reference mass spectrum from the NBS database (NBS75K.I). This database is used as it contains relatively uncontaminated mass spectra of each target compound which cannot be obtained from the daily calibrations during each 12 hour analytical period due to overlapping peaks in the mixes. Characteristic ions from the reference mass spectrum library are defined as the three ions of greatest relative intensity, or any ions over 30% relative intensity, if less than three such ions occur in the reference spectrum. In addition, the following criteria must be met. The RRT of the sample analyte must be within 0.06 RRT units of the RRT of the standard analyte. The relative intensities of the characteristic ions must agree within 30% of the relative intensities of the same ions in the reference spectrum. Structural isomers that produce very similar mass spectra should be identified as individual isomers so long as their GC retention times differ substantially. A library search may be made for analytes not associated with the calibration for the purpose of tentative identification. NOTE: The GC/MS analyst uses intelligence guided by experience to make the identifications. In uncontaminated spectra where ions are missing due to low concentration, if the major ions are present in the correct ratios at the correct retention time, the identification will be considered positive. In contaminated spectra, special emphasis will be placed upon higher mass ions, and the major ions will usually need to be present as major components of the spectrum (either unsubtracted or subtracted) for the identification to be positive. All assessments of relative intensities of ions will be made by visual estimates from the spectra.

7.9.5 Quantitation - Once a compound has been identified qualitatively, the concentration must then be quantitated. If the RSD of the compound's response factor is 15% or less, then the concentration may be determined using the average response factor ($\overline{RF}$) from the initial calibration data. Otherwise, the concentration must be determined from equations based on internal standard calibration using either linear or non-linear calibration. Calculations follow in Section 7.10.

7.10 Calculations:

7.10.1 The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.

A_{is} = Peak area (or height) of the internal standard.

C_s = Concentration of the analyte or surrogate.

C_{is} = Concentration of the internal standard.

7.10.2 Calibration verification involves the calculation of the percent drift (linear or quadratic) or the percent difference (average) of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference, depending on the calibration procedure used.

$$\% \text{ Drift} = \frac{(\text{Calculated concentration} - \text{Theoretical concentration}) * 100}{\text{Theoretical Concentration}}$$

where the calculated concentration is determined from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{(\text{CCV RF} - \text{Average RF}) * 100}{\text{Average RF}}$$

where CCV RF is the response factor from the analysis of the verification standard and Average RF is the average response factor from the initial calibration. The % difference or % drift calculated for the calibration verification standard must be within ±20% for each CCC analyte, or for all target analytes if the CCCs are not target analytes, before any sample analyses may take place.

7.10.3 Concentration in water samples is calculated as follows: [Note: Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.]

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(V_s)(1000)}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

A_{is} = Area (or height) of the peak for the internal standard.

C_{is} = Concentration of the internal standard in the volume extracted in ug/L.

D = Dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

V_i = Volume of the extract injected (µL). The nominal injection volume for samples and calibration standards must be the same.

$\overline{RF}$ = Mean response factor from the initial calibration.

V_s = Volume of the aqueous sample extracted (mL). If units of liters are used for this term, multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL. If the injection (V_i) is expressed in mL, then the 1000 may be omitted.

7.10.4 Concentration in non-aqueous samples is calculated as follows: [Note: Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.]

7.10.5

$$\text{Concentration } (\mu\text{g/kg}) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(W_s)(1000)}$$

where: A_s,

A_{is}, C_{is}, D, and $\overline{RF}$ are the same as for aqueous samples, and

W_s = Weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL. If the injection (V_i) is expressed in mL, then the 1000 may be omitted.

8.0 QUALITY ASSURANCE/QUALITY CONTROL/CORRECTIVE ACTIONS

8.1 Internals - All samples and QC are spiked with internal standards. See section 7.7.1 above for criteria and corrective action.

8.2 Surrogates - All samples and QC are spiked with surrogates. The surrogate recoveries from method blanks and LCS are used to generate control control limits for the surrogates. See section 7.9.2 above for criteria and corrective action. If any surrogate recoveries are below 10%, samples must be re-extracted if sample is available.

8.3 LCS Sample - The LCS is extracted 1 per extraction batch of up to 20 samples. The LCS is spiked using an alternate source or lot number than the calibration standards. If the LCS compound has a recovery above the upper limit, but the same compound is not detected in any of the batch samples, no corrective action is required. For all other situations, the LCS should be reanalyzed for the failed analytes only. If the second analysis fails, all associated samples should be reextracted/reanalyzed for the failed analytes only or the data must be evaluated for flagging due to QC problems.

8.4 Method Blanks - The concentration of all method target analytes should be below the MDL for each method target analyte(**<RL for common lab contaminants and <1/2 RL for other targets for DOD QSM Ver.3 projects**). The first step of corrective action is to assess the effect on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps should be taken to find/reduce/eliminate the source of this contamination in the method blank. If an analyte is found in the method blank and some, or all, of the other batch samples, then corrective action is required. The source of contamination must be investigated and appropriate action taken and documented to find/reduce/eliminate the source of this contamination. The method blank, and any samples containing the same contaminant, may need to be reextracted/reanalyzed. For the common laboratory contaminants, meeting the above

requirements is not practical. Random cases of contamination are difficult to control, however, daily contamination is not acceptable and corrective action is essential. If a contaminant is found in the method blank and the samples, the compound concentration must be flagged with a 'B' on the final report unless the concentration is greater than 10x that found in the method blank.

8.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample - 1 in 20 samples are spiked for a MS/MSD (for full list spikes, the full list spiking solution is used). Control limits for the MS/MSD recoveries are the same as those for the LCS found in the appendix. RPD limits are found on the LCS report forms in the appendix. Samples which do not meet these criteria due to matrix must be evaluated for flagging on the final report due to QC problems. Generally, batch control is not based on MS/MSD results unless general method failure is determined to be the problem. In that case, the samples and associated QC would be reanalyzed for the failed analytes only. MS data evaluation must include the consideration of the following factors.

8.5.1 Sample matrix - If the sample is a soil, grab sample or sequentially collected water sample it may affect the %R and RPD of the MS/MSD. Corrective action must be taken in the form of reanalysis if a method problem is indicated.

8.5.2 Original sample concentration - If a spiked compound has a problem and the concentration of that compound in the original sample was two or more times the concentration of the spike, no further corrective action may be necessary other than the generation of a corrective action report to document the problem.

8.5.3 MS vs. MSD - If a spiked compound has a similar problem in both the MS and MSD and is not traced to a method problem, no further action may be necessary other than the generation of a corrective action report to document the problem.

8.5.4 Non-target Interference - The presence of significant non-target interference should be brought to the immediate attention of your supervisor who should discuss the problem with the client/project manager to determine the action to be taken.

8.5.5 Documentation of Capability (DOC) – Each analyst must perform a DOC to demonstrate proficiency with the method. Refer to SOP-413 for guidance.

9.0 HEALTH AND SAFETY

9.1 Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of gloves and lab coats is highly recommended.

9.2 Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples which need special consideration have applicable notes on the sample logs.

9.3 MSDS sheets are available for all reagents and standards which have been purchased. These are located on the bookshelf outside the office supply storage room.

10.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

10.1 Please see Waste Disposal, SOP-210 and SOP-405 for proper disposal of waste coming from this area within our laboratory.

10.2 Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

11.0 TABLE OF DEFINITIONS, REFERENCES & EXAMPLE FORMS

Definitions and examples of the LCS report sheets (625 water limits, in-house water limits and in-house soil limits), the analyst data review checklist and figure 13 from *Federal Register* method 625 for the tailing factor calculation are located in the appendix.

APPENDIX

TABLE OF DEFINITIONS

1. amu- atomic mass unit
2. BNA- Base neutral/acid
3. °C- degrees Centigrade
4. CCC- Calibration Check Compound
5. CCV- Continuing Calibration Verification
6. CLP- Contract Laboratory Program
7. %D- percent difference
8. DFTPP- Difluorotriphenyphosphine
9. EICP- extracted ion current profile
10. EPA- Environmental Protection Agency
11. g- gram or grams
12. GC- Gas Chromatograph
13. GC/MS- Gas Chromatograph/Mass Spectrometer
14. ICV- Initial Calibration Verification
15. I.D.- inner diameter
16. ISTD- internal standard
17. LSC- Laboratory Sample Concentrator
18. MDL- method detection limit
19. MS- Matrix Spike
20. MSD- Matrix Spike Duplicate
21. M.S.- Mass Spectrometer
22. µm- micometer
23. µL- microliter
24. mL- milliliter
25. mm- millimeter
26. ng- nanogram
27. NPDES- National Pollutant Discharge Elimination System
28. P&T- purge and trap
29. QC- quality control
30. %R- percent recovery
31. RPD- relative percent difference
32. RRT- relative retention time
33. %RSD- percent relative standard deviation
34. SOP- Standard Operating Procedure
35. Surr.- surrogate
36. SPCC- System Performance Check Compound
37. TCLP- Toxicity Characteristic Leaching Procedure
38. USACE- United States Army Corps Of Engineers
39. LCS – Lab Control Sample

REFERENCES

1. *40 CFR, Part 136*; Appendix A
2. *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition
3. *National Environmental Laboratory Accreditation Conference*; CH. 5, 2001
4. USACE, *EM 200-1-3; Appendix 1; Shell*, 2/2001
5. *DOD Quality Systems Manual for Environmental Laboratories*, 6/2002

FORM 3

WATER SEMIVOLATILE LAB CONTROL SAMPLE (625)

Lab Name: Empirical Laboratories Contract:

Lab Code: NA Batch No.: NA SAS No.: NA SDG No.:

Matrix Spike - Client Sample No.:

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	LCS CONCENTRATION (ug/L)	LCS % REC #	QC. LIMITS REC.
Acenaphthene	100.00	0.0000	100.00	100	47-145
Acenaphthylene	100.00	0.0000	100.00	100	33-145
Anthracene	100.00	0.0000	100.00	100	27-133
Benzidine	100.00	0.0000	100.00	100	D-110
Benzo(a)anthracene	100.00	0.0000	100.00	100	33-143
Benzo(b)fluoranthene	100.00	0.0000	100.00	100	24-159
Benzo(k)fluoranthene	100.00	0.0000	100.00	100	11-162
Benzo(g,h,i)perylene	100.00	0.0000	100.00	100	D-219
Benzo(a)pyrene	100.00	0.0000	100.00	100	17-163
bis(2-Chloroethoxy)meth	100.00	0.0000	100.00	100	33-184
bis(2-Chloroethyl)ether	100.00	0.0000	100.00	100	12-158
bis(2-Chloroisopropyl)e	100.00	0.0000	100.00	100	36-166
Bis(2-ethylhexyl)phthal	100.00	0.0000	100.00	100	8-158
4-Bromophenyl-phenyleth	100.00	0.0000	100.00	100	53-127
Butylbenzylphthalate	100.00	0.0000	100.00	100	D-152
4-Chloro-3-methylphenol	100.00	0.0000	100.00	100	22-147
2-Chloronaphthalene	100.00	0.0000	100.00	100	60-118
2-Chlorophenol	100.00	0.0000	100.00	100	23-134
4-Chlorophenyl-phenylet	100.00	0.0000	100.00	100	25-158
Chrysene	100.00	0.0000	100.00	100	17-168
Dibenz(a,h)anthracene	100.00	0.0000	100.00	100	D-227
1,2-Dichlorobenzene	100.00	0.0000	100.00	100	32-129
1,3-Dichlorobenzene	100.00	0.0000	100.00	100	D-172
1,4-Dichlorobenzene	100.00	0.0000	100.00	100	20-124
3,3'-Dichlorobenzidine	100.00	0.0000	100.00	100	D-262
2,4-Dichlorophenol	100.00	0.0000	100.00	100	39-135
Diethylphthalate	100.00	0.0000	100.00	100	D-114
2,4-Dimethylphenol	100.00	0.0000	100.00	100	32-119

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

COMMENTS: _____

FORM 3

WATER SEMIVOLATILE LAB CONTROL SAMPLE (625)

Lab Name: Empirical Laboratories Contract:

Lab Code: NA Batch No.: NA SAS No.: NA SDG No.:

Matrix Spike - Client Sample No.:

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	LCS CONCENTRATION (ug/L)	LCS % REC #	QC. LIMITS REC.
Dimethylphthalate	100.00	0.0000	100.00	100	D-112
Di-n-butylphthalate	100.00	0.0000	100.00	100	1-118
4,6-Dinitro-2-methylphe	100.00	0.0000	100.00	100	D-181
2,4-Dinitrophenol	100.00	0.0000	100.00	100	D-191
2,4-Dinitrotoluene	100.00	0.0000	100.00	100	39-139
2,6-Dinitrotoluene	100.00	0.0000	100.00	100	50-158
Di-n-octylphthalate	100.00	0.0000	100.00	100	4-146
Fluoranthene	100.00	0.0000	100.00	100	26-137
Fluorene	100.00	0.0000	100.00	100	59-121
Hexachlorobenzene	100.00	0.0000	100.00	100	D-152
Hexachlorobutadiene	100.00	0.0000	100.00	100	24-116
Hexachlorocyclopentadie	100.00	0.0000	100.00	100	15- 70
Hexachloroethane	100.00	0.0000	100.00	100	40-113
Indeno(1,2,3-cd)pyrene	100.00	0.0000	100.00	100	D-171
Isophorone	100.00	0.0000	100.00	100	21-196
Naphthalene	100.00	0.0000	100.00	100	21-133
Nitrobenzene	100.00	0.0000	100.00	100	35-180
2-Nitrophenol	100.00	0.0000	100.00	100	29-182
4-Nitrophenol	100.00	0.0000	100.00	100	D-132
N-Nitroso-di-methylamin	100.00	0.0000	100.00	100	29- 66
N-Nitrosodiphenylamine	100.00	0.0000	100.00	100	23-100
N-Nitroso-di-n-propylam	100.00	0.0000	100.00	100	D-230
Pentachlorophenol	100.00	0.0000	100.00	100	14-176
Phenanthrene	100.00	0.0000	100.00	100	54-120
Phenol	100.00	0.0000	100.00	100	5-112
Pyrene	100.00	0.0000	100.00	100	52-115
1,2,4-Trichlorobenzene	100.00	0.0000	100.00	100	44-142
2,4,6-Trichlorophenol	100.00	0.0000	100.00	100	37-144

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

RPD: 0 out of 0 outside limits
Spike Recovery: 0 out of 56 outside limits

COMMENTS: _____

FORM 3

WATER SEMIVOLATILE LAB CONTROL SAMPLE (In-House)

Lab Name: Empirical Laboratories Contract:

Lab Code: NA Batch No.: NA SAS No.: NA SDG No.:

Matrix Spike - Client Sample No.:

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	LCS CONCENTRATION (ug/L)	LCS % REC #	QC. LIMITS REC.
Acenaphthene	100.0	0.0000	100.00	100	40-112
4-Chloro-3-methylphenol	200.0	0.0000	200.00	100	32-110
2-Chlorophenol	200.0	0.0000	200.00	100	29-110
1,4-Dichlorobenzene	100.0	0.0000	100.00	100	26-110
2,4-Dinitrotoluene	100.0	0.0000	100.00	100	46-122
4-Nitrophenol	200.0	0.0000	200.00	100	21-110
N-Nitroso-di-n-prop.(1)	100.0	0.0000	100.00	100	39-110
Pentachlorophenol	200.0	0.0000	200.00	100	32-133
Phenol	200.0	0.0000	200.00	100	10-110
Pyrene	100.0	0.0000	100.00	100	51-137
1,2,4-Trichlorobenzene	100.0	0.0000	100.00	100	28-110

COMPOUND	SPIKE ADDED (UG/L)	MSD CONCENTRATION (UG/L)	MSD % REC #	% RPD #	QC LIMITS RPD	QC LIMITS REC.
Acenaphthene	100.0	100.00	100	0	31	40-112
4-Chloro-3-methylphenol	200.0	200.00	100	0	42	32-110
2-Chlorophenol	200.0	200.00	100	0	40	29-110
1,4-Dichlorobenzene	100.0	100.00	100	0	28	31-110
2,4-Dinitrotoluene	100.0	100.00	100	0	38	46-122
4-Nitrophenol	200.0	200.00	100	0	50	21-110
N-Nitroso-di-n-prop.(1)	100.0	100.00	100	0	38	39-110
Pentachlorophenol	200.0	200.00	100	0	50	32-133
Phenol	200.0	200.00	100	0	42	10-110
Pyrene	100.0	100.00	100	0	31	51-137
1,2,4-Trichlorobenzene	100.0	100.00	100	0	28	28-110

(1) N-Nitroso-di-n-propylamine
Column to be used to flag recovery and RPD values with an asterisk
* Values outside of QC limits

RPD: 0 out of 11 outside limits
Spike Recovery: 0 out of 22 outside limits

COMMENTS: _____

FORM 3

SOIL SEMIVOLATILE LAB CONTROL SAMPLE (In-House)

Lab Name: Empirical Laboratories Contract:

Lab Code: ELABN Case No.: NA SAS No.: NA SDG No.:

Matrix Spike - Client Sample No.: Level:(low/med) LOW

COMPOUND	SPIKE ADDED (ug/Kg)	SAMPLE CONCENTRATION (ug/Kg)	LCS CONCENTRATION (ug/Kg)	LCS % REC #	QC. LIMITS REC.
Acenaphthene	10000	0.0000	10000	100	27-116
4-Chloro-3-methylphenol	20000	0.0000	20000	100	18-111
2-Chlorophenol	20000	0.0000	20000	100	10-110
1,4-Dichlorobenzene	10000	0.0000	10000	100	14-110
2,4-Dinitrotoluene	10000	0.0000	10000	100	34-110
4-Nitrophenol	20000	0.0000	20000	100	24-120
N-Nitroso-di-n-prop.(1)	10000	0.0000	10000	100	24-112
Pentachlorophenol	20000	0.0000	20000	100	10-114
Phenol	20000	0.0000	20000	100	10-110
Pyrene	10000	0.0000	10000	100	33-150
1,2,4-Trichlorobenzene	10000	0.0000	10000	100	19-110

COMPOUND	SPIKE ADDED (ug/Kg)	LCSD CONCENTRATION (ug/Kg)	LCSD % REC #	% RPD #	QC LIMITS RPD	QC LIMITS REC.
Acenaphthene	10000	10000	100	0	19	27-116
4-Chloro-3-methylphenol	20000	20000	100	0	42	18-111
2-Chlorophenol	20000	20000	100	0	50	10-110
1,4-Dichlorobenzene	10000	10000	100	0	27	14-110
2,4-Dinitrotoluene	10000	10000	100	0	47	34-110
4-Nitrophenol	20000	20000	100	0	50	24-120
N-Nitroso-di-n-prop.(1)	10000	10000	100	0	38	24-112
Pentachlorophenol	20000	20000	100	0	47	40-110
Phenol	20000	20000	100	0	35	10-110
Pyrene	10000	10000	100	0	36	33-150
1,2,4-Trichlorobenzene	10000	10000	100	0	23	19-110

(1) N-Nitroso-di-n-propylamine
Column to be used to flag recovery and RPD values with an asterisk
* Values outside of QC limits
RPD: 0 out of 11 outside limits
Spike Recovery: 0 out of 22 outside limits

COMMENTS: _____

BNA STANDARDS USED

base/neutral mix (2000ppm)		**acids mix (2000ppm)**
bis(2-Chloroethyl)ether		2,4-Dinitrophenol
bis(2-Chloroisopropyl)ether		2-Methylphenol
1,3-Dichlorobenzene		4-Methylphenol
1,2-Dichlorobenzene		Benzoic acid
1,4-Dichlorobenzene		4,6-Dinitro-2-methylphenol
Hexachloroethane		4-Nitrophenol
N-Nitroso-di-methylamine		2,4,5-Trichlorophenol
N-Nitroso-di-n-propylamine		2,4,6-Trichlorophenol
2,4-Dinitrotoluene		Phenol
2,6-Dinitrotoluene		Pentachlorophenol
Fluorene		2-Nitrophenol
Dimethylphthalate		4-Chloro-3-methylphenol
Hexachlorocyclopentadiene		2,4-Dichlorophenol
Anthracene		2,4-Dimethylphenol
4-Bromophenyl-phenylether		Benzoic acid
Di-n-butylphthalate		
bis(2-Chloroethoxy)methane		
1,2-Diphenylhydrazine		**semivoa misc.mix(2000ppm)**
Fluoranthene		Aniline
Hexachlorobenzene		Benzyl alcohol
N-Nitrosodiphenylamine		Carbazole
Phenanthrene		4-Chloroaniline
Hexachlorobutadiene		Dibenzofuran
Isophorone		2-Methylnaphthalene
Naphthalene		2-Nitroaniline
Nitrobenzene		3-Nitroaniline
1,2,4-Trichlorobenzene		4-Nitroaniline
Acenaphthene		Pyridine
Acenaphthylene		
2-Chloronaphthalene		
4-Chlorophenyl-phenylether		**Benzidine mix (2000ppm)**
Diethylphthalate		Benzidine
Benzo(a)anthracene		3,3'-Dichlorobenzidine
Bis(2-ethylhexyl)phthalate		
Butylbenzylphthalate		
Chrysene		**individual mixes (10,000ppm)**
p-(Dimethylamino)azobenzene		Caprolactam
Pyrene		Benzaldehyde
Benzo(b)fluoranthene		Atrazine
Benzo(k)fluoranthene		1,1'-Biphenyl
Benzo(g,h,i)perylene		Catechol
Benzo(a)pyrene		
Dibenz(a,h)anthracene		
Di-n-octylphthalate		
Indeno(1,2,3-cd)pyrene		

INTERNAL STANDARD ASSOCIATION / QUANT ION TABLE					
COMPOUND	***I.S**	**Q.M**	**COMPOUND**	***I.S**	**Q.M**
1,4-Dichlorobenzene-d4 **(I.S)(1)**		152	Dimethylphthalate	59	163
Acetophenone	1	105	Hexachlorocyclopentadiene	59	237
Aniline	1	93	2,4-Dinitrophenol	59	184
Benzaldehyde	1	106	2,4-Dinitrotoluene	59	165
Benzyl alcohol	1	108	2,6-Dinitrotoluene	59	165
bis(2-Chloroethyl)ether	1	93	Fluorene	59	166
bis(2-Chloroisopropyl)ether	1	45	2-Nitroaniline	59	65
1,3-Dichlorobenzene	1	146	3-Nitroaniline	59	138
1,2-Dichlorobenzene	1	146	4-Nitroaniline	59	138
1,4-Dichlorobenzene	1	146	4-Nitrophenol	59	65
2-Methylphenol	1	108	2,4,5-Trichlorophenol	59	196
4-Methylphenol	1	108	2,4,6-Trichlorophenol	59	196
3-Methylphenol	1	108	2-Fluorobiphenyl (S)	59	172
Phenol	1	94	Phenanthrene-d10 **(I.S) (79)**		188
Pyridine	1	79	Anthracene	79	178
Hexachloroethane	1	117	Atrazine	79	200
N-Nitroso-di-methylamine	1	42	4-Bromophenyl-phenylether	79	248
N-Nitroso-di-n-propylamine	1	70	Carbazole	79	167
2-Fluorophenol (S)	1	112	Di-n-butylphthalate	79	149
Phenol-d6 (S)	1	99	4,6-Dinitro-2-methylphenol	79	198
Naphthalene-d8 **(I.S)(35)**		136	1,2-Diphenylhydrazine	79	77
Benzoic acid	35	105	Fluoranthene	79	202
bis(2-Chloroethoxy)methane	35	93	Hexachlorobenzene	79	284
Caprolactam	35	113	N-Nitrosodiphenylamine	79	169
4-Chloroaniline	35	127	Pentachlorophenol	79	266
4-Chloro-3-methylphenol	35	107	Phenanthrene	79	178
2,4-Dichlorophenol	35	162	2,4,6-Tribromophenol (S)	79	330
2,4-Dimethylphenol	35	107	Chrysene-d12 **(I.S) (92)**		240
Hexachlorobutadiene	35	225	Benzidine	92	184
Isophorone	35	82	Benzo(a)anthracene	92	228
2-Methylnaphthalene	35	141	Bis(2-ethylhexyl)phthalate	92	149
Naphthalene	35	128	Butylbenzylphthalate	92	149
Nitrobenzene	35	77	Chrysene	92	228
2-Nitrophenol	35	139	3,3'-Dichlorobenzidine	92	252
1,2,4-Trichlorobenzene	35	180	p-(Dimethylamino)azobenzene	92	225
Catechol	35	110	Pyrene	92	202
Nitrobenzene-d5 (S)	35	82	Terphenyl-d14 (S)	92	244
Acenaphthene-d10 **(I.S) (59)**		164	Perylene-d12 **(I.S) (101)**		264
Acenaphthene	59	153	Benzo(b)fluoranthene	101	252
Acenaphthylene	59	152	Benzo(k)fluoranthene	101	252
1,1'-Biphenyl	59	154	Benzo(g,h,i)perylene	101	276
2-Chloronaphthalene	59	162	Benzo(a)pyrene	101	252
4-Chlorophenyl-phenylether	59	204	Dibenz(a,h)anthracene	101	278
Dibenzofuran	59	168	Di-n-octylphthalate	101	149
Diethylphthalate	59	149	Indeno(1,2,3-cd)pyrene	101	276
I.S=internal standard, Q.M=quant mass, S=surrogate					

INTERNAL STANDARD ASSOCIATION / QUANT ION TABLE					
COMPOUND	***I.S**	**Q.M**	**COMPOUND**	***I.S**	**Q.M**
1,4-Dichlorobenzene-d4 **(I.S)(1)**		152	Diphenylamine	59	169
Pentachloroethane	1	167	Thionazin	59	107
2-Picoline	1	93		59	
N-Nitrosomethylethylamine	1	88		59	
Methyl methanesulfonate	1	80		59	
N-Nitrosodiethylamine	1	102		59	
Ethyl methanesulfonate	1	79		59	
N-Nitrosopyrrolodine	1	100		59	
N-Nitrosomorpholine	1	56		59	
0-Toluidine	1	106		59	
	1			59	
	1			59	
	1			59	
	1		Phenanthrene-d10 **(I.S) (79)**		188
	1		4-Nitroquinoline-1-oxide	79	190
	1		Phenacetin	79	108
	1		4-Aminobiphenyl	79	169
	1		Pentachloronitrobenzene	79	237
	1		Sulfotepp	79	97
	1		Phorate	79	75
Naphthalene-d8 **(I.S)(35)**		136	Diallate	79	86
1- Methylnaphthalene	35	141	Dimethoate	79	87
N-Nitrosopiperidine	35	114	Pronamide	79	173
a,a-Dimethylphenethylamine	35	58	Disulfoton	79	88
O,O,O-Triethylphosphorothioate	35	97	Dinoseb	79	211
Hexachloropropene	35	213		79	
2,6-Dichlorophenol	35	162		79	
p-Phenylenediamine	35	108	Chrysene-d12 **(I.S) (92)**		240
N-Nitrosodi-n-butylamine	35	84	Methapyrilene	92	97
Safrole	35	162	p-(Dimethylamino)azobenzene	92	225
1,2,4,5-Tetrachlorobenzene	35	216	Chlorobenzilate	92	251
	35		3,3'- Dimethylbenzidine	92	212
	35		2- Acetylaminofluorene	92	181
	35		7,12-Dimethylbenz[a]anthracene	92	256
	35		Aramite	92	185
	35		Methyl parathion	92	109
	35		Parathion	92	109
Acenaphthene-d10 **(I.S) (59)**		164	Isodrin	92	193
Isosafrole	59	162	Kepone	92	272
1,4-Naphthoquinone	59	158	Famphur	92	218
Pentachlorobenzene	59	250	Perylene-d12 **(I.S) (101)**	101	
2-Naphthylamine	59	143	3-Methylcholanthrene	101	268
1-Naphthylamine	59	143	Hexachlorophene	101	196
2,3,4,6-Tetrachlorophenol	59	232		101	
5-Nitro-o-toluidine	59	152		101	
I.S=internal standard, Q.M=quant mass, S=surrogate					

Internal Standards & Surrogates

BNA internals (2000ppm)	**Acid surrogate (7500ppm)**
1,4-Dichlorobenzene-d4 **(I.S)(1)**	2-Fluorophenol (S)
Naphthalene-d8 **(I.S)(35)**	Phenol-d6 (S)
Acenaphthene-d10 **(I.S) (59)**	2,4,6-Tribromophenol (S)
Phenanthrene-d10 **(I.S) (79)**	**2,-Chlorophenol-d4 (S)**
Chrysene-d12 **(I.S) (92)**	
Perylene-d12 **(I.S) (101)**	**BN surrogate (5000ppm)**
	Nitrobenzene-d5 (S)
	Terphenyl-d14 (S)
	2-Fluorobiphenyl (S)
	1,2-Dichlorobenzene-d4 (S)

ANALYST DATA REVIEW CHECKLIST

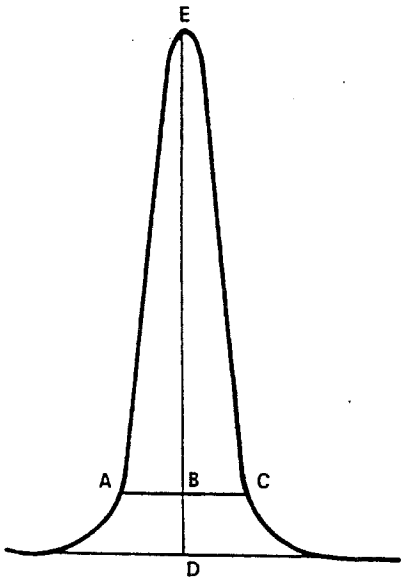
Sample Number(s):	
Batch Number(s):	
Method:	**8260B/8270C (Circle One)**

QA/QC Item	Yes	No	NA	Second Level Review
1. Is the BFB/DFTPP tune performed every 12 hours and is the tuning criteria met?				
2. Are the RRFs and % RSDs within QC limits for appropriate analytes for the initial calibration? Check the retention times for compounds with the same spectra. Check compounds with different conc.(eg. m/p-xylene, ketones,etc.).				
3. Was the initial calibration curve verified by a second source calibration standard (ICV) and have criteria been met?				
4. Does the Continuing Calibration Standard (CCV) meet the criteria for the CCCs and SPCCs.				
5. Is the Method Blank run at the desired frequency and is its concentration for target analytes less than the MDLs?				
6. Are the LCS, MS, MSD within control limits and run at the desired frequency?				
7. Are all sample holding times met, analytes within calibration range, IS areas and surrogate recoveries within QC limits?				
8. Was the Method Blank, LCS, MS, MSD and samples loaded to the GCMS_LFSYS Tablespace within the Target DB Database?				

Comments on any "No" response:

Primary-Level Review: _____ Date: _____

Second-Level Review: _____ Date: _____



TAILING FACTOR= $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

Figure 13. Tailing factor calculation.

[Part 136, Appendix A, Method 625]

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GC/MS VOLATILES
BY EPA METHOD 624 AND
SW-846 METHOD 8260B
INCLUDING APPENDIX IX COMPOUNDS

SOP NUMBER: SOP-202

REVISION NUMBER: 19

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: 09/29/06

DATE OF LAST REVIEW 09/29/06

GC/MS VOLATILES
BY EPA METHOD 624 AND SW-846 METHOD 8260B

1.0 SCOPE AND APPLICATION

Please see Appendix for definitions.
This SOP (based primarily on SW-846 Method 8260B) is used for the analysis of volatile organic compounds in a variety of matrices (soils, sediments, waters, etc.). Methods SW-846 Method 8000B; *Federal Register* Method 624; and CLP Method for Volatiles have also been used in the development of this SOP. The analyses by these various methods are clearly defined in the respective regulatory manuals. A good understanding of these different methods is essential to the performance of each method. The normal laboratory list of analytes with their typical LCS limits is found attached in the appendix. Other compounds may be analyzed by this SOP as detailed in section 1.0 of SW-846 Method 8260B. Any questions left by this SOP should be answered by reading the methods, paying close attention to SW-846 8000B/8260B, EPA 624 and CLP. If questions still remain unanswered, check with the Organic Lab Manager, QA/QC Officer and/or the Technical Director.

2.0 METHOD SUMMARY

After sample preparation, the sample is introduced into the GC/MS generally using purge and trap but sometimes using direct injection (see SW-846 Methods 5030B, 5035 and 3585 for preparation). In purge and trap, the analytes are stripped from the sample using helium and trapped on an adsorbent tube. The tube is heated while being backflushed with helium to carry the analytes to the GC/MS system. The analytes are separated in the gas chromatograph by a combination of the temperature program and the capillary column. The analytes are then detected by the mass spectrometer. Analytes are identified by comparing the mass spectra of known standards with the mass spectra of the sample. Analytes are quantitated relative to known standards using the internal standard method.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Section 7.0 and tables 6-1 and 6-2 of the Empirical Laboratories, LLC Quality Assurance Manual include details concerning sample preservation, containers and handling of volatile samples. All water and non-quarantined soil volatile samples are stored in the Hobart in the sample storage room at a temperature of 4°C. Quarantined soil volatile samples are stored in the dorm-size refrigerator in the sample receiving/log-in room at a temperature of 4°C. Non-preserved water volatile samples have a holding time of 7 days from date of sampling. Preserved water samples and soil volatile samples have a holding time of 14 days from date of sampling (unless otherwise specified for the project).

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Section 3.0 of SW-846 Method 8260B details interferences and potential problems which may be encountered when dealing with volatile analyses.

5.0. EQUIPMENT AND APPARATUS

5.1 GC : HP 5890 or 6890, temperature programmable, suitable for split or splitless injection.

5.2 Column: DB-VRX 60 meter x 0.25 mm I.D. 1.4 µm film thickness or 20 meter x 0.18 mm ID 1.0 µm film thickness silicon coated fused silica capillary column.

5.3 M.S. : HP 5971, 5972 or 5973 capable of scanning 35 to 500 amu every one second or less, using 70 volts electron energy in electron impact ionization mode. The MS is capable of producing a mass spectrum for p-Bromofluorobenzene, BFB, which meets all tuning criteria for EPA methods [when 1 µL (50 ng) of the GC/MS tuning standard are injected through the GC.]

5.4 Purge and Trap Unit

5.4.1 Concentrators: Tekmar LSC 2000 or Tekmar/Dohrmann 3100 Sample Concentrator equipped with Supelco trap number 2-1066-U or 2-4920-U VOCARB 3000 providing good delivery for all target compounds.

5.4.2 Autosamplers: Varian Archon 51 position programmable autosampler with 5ml to 25ml water and heated soil capability.

5.5 Acquisition Software: HP chemstation system interfaced to the GC/MS. The system acquires and stores data throughout the chromatographic programs.

5.6 Data Processing Software: TargetDB on Windows NT data system interfaced to the HP Chemstation. The system accepts and stores acquired data. It plots by extracted ion current profile (EICP). The system is also capable of integrating the abundances of any EICP between specified time or scan-number limits. The most recent NBS mass spectral library is installed.

5.7 Microsyringes – 1.0, 5.0,10, 25, 100, 250, 500 and 1000 µL.

5.8 Syringes – 5, 25 and 50 mL, gas-tight with Luer end.

5.9 Balance - analytical, 0.0001 g; top-loading, 0.1 g.

5.10 Disposable pasteur pipets.

5.11 Volumetric flasks, Class A - 2 mL, 5 mL, 10 mL, 50 mL, 100 mL and 250 mL with ground-glass stoppers.

5.12 Spatula - stainless steel.

5.13 Glass scintillation vials - 20mL with screw caps.

5.14 Purple Nitrile Gloves

5.15 pH paper (measures pH from 0-14).

6.0 REAGENTS AND SOLUTIONS

6.1 Organic-free reagent water - obtained from a modulab system.

6.2 Methanol - Purge and trap grade (EM-Omnisolv EM-0482-6 or equivalent)

6.3 Methanol - suitable for use in gas chromatography (B&J Omnisolv MX0484-1, or equivalent)

6.4 Sodium bisulfate, $NaHSO_4$ – ACS reagent grade, or equivalent. Available from Aldrich (Part No. 30,782-3).

6.5 Stock standards are purchased in mixtures from reputable vendors. The date they are received is noted on the label. The date they are opened is noted on the label and recorded in the VOA standards and reagents logbook along with their lot number and vendor. Each standard that is prepared is recorded in the VOA standards and reagents logbook and given a sequential number. Each standard label is completed with the standard number, name, preparation date, expiration date, solvent and analyst initials. Stock standards, when opened, have an expiration date of 6 months except for gas standards for South Carolina samples which have a one week expiration date. All stocks and standards are stored in the freezer at a temperature of -15°C ± 5°C or less from the date they are received/prepared. The freezer temperature is monitored daily with an annually calibrated thermometer and recorded with calibration correction in the VOA refrigerator/freezer logbook. Makeup of common standards is detailed below. See the VOA standards log book for makeup of other standards.

6.5.1 The Bromofluorobenzene (BFB) tuning standard is prepared as follows: Using a 50µL syringe, 40µL of standard (BFB @ 2500ng/µL) is injected into a 2mL volumetric flask containing approximately 1.0mL P&T methanol (Vendor,Lot) and diluted to volume with same making a 50ng/µL standard. After capping and inverting 3 times, the solution is transferred to a labeled 2ml, teflon-lined, screw-capped vial and stored in the freezer at -15°C ± 5°C or less for up to 6 months(1 week for South Carolina samples). A direct injection of 1µL is used to tune the instrument.

6.5.2 The internal and surrogate standard is prepared as follows: Using the indicated syringe, the indicated amount of standard is injected into a 50 mL volumetric flask containing P&T methanol (Vendor,Lot) and diluted to volume with same making a 150ng/µL standard. After capping and inverting 3 times, the solution is transferred to the Archon standard vial and stored under helium for 1 month or less. Each 8260/624 sample is automatically injected with 1µL of this standard. The internal standard/surrogate solution will be replaced if the –50%-200% criteria fails in the CCV.

Standard	Conc. (ng/µL)	Syringe (µL)	Amount (µL)
8260 ISTD/Surr. Mix (Vendor,Lot)	2500	1000	3000

6.5.3 Calibration standards are prepared from the vendor stock standards at appropriate concentrations as follows. Occasionally unusual compounds are added to the mix so it is best to check the VOA standards log book for exact standard makeup. Note: for laboratory control spikes (LCS), alternate sources or lot numbers from the main calibration standard are used to make the LCS standard. See the appendix for analytes in the main mixes.

6.5.3.1 Primary Standard: Using the indicated syringe, the indicated amount of standard is injected into a 2mL volumetric flask containing approximately 1.0mL P&T methanol (Vendor,Lot) and diluted to volume with same to make a 100-500ng/µL standard. After capping and inverting 3 times, the solution is transferred into 2ml amber vial w/mini-inert valve and stored in the freezer at -15°C ± 5°C for 1 week. A 50µg/L (5mL purge) standard is made using 25µL of this standard to 50mLof reagent water.

Stock Standard(CCV)	Conc (ng/µL)	Syringe(µL)	Amount(µL)	Final Conc (ng/µL)
2-CEVE (Cat#30265) (Vendor, Lot)	20000	25	20	200
Vinyl Acetate (#3766) (Vendor, Lot)	5000	100	80	200
Ketones (cat#30006) (Vendor, Lot)	5000	100	80	200
Liquid mix (C-349H-07) (Vendor, Lot)	2000	100	100	100
Custom mix (CCS-1037) (Vendor, Lot)	5000	50	40	100
Gases (cat#30042) (Vendor, Lot)	2000	100	100	100
Acrolein/Acrylonitrile (CC2098.10) (Vendor, Lot)	20,000	50	50	500

Additional compounds may be added such as Appendix IX. Refer to standards log.

6.5.4 ICV/LCS/MATRIX SPIKE MIX: A second source standard is to check the validity of the gas and primary calibration standards used in analyzing the calibration curve. Using the indicated syringe, the indicated amount of standard is injected into a 2mL volumetric flask containing approximately 1.0mL P&T methanol (Vendor,Lot) and diluted to volume with same to make a 100-500ng/µL standard. After capping and inverting 3 times, the solution is transferred into 2ml amber vial w/mini-inert valve and stored in the freezer at -15°C ± 5°C for 1 week. A 50µg/L (5mL purge) ICV/LCS/Matrix Spike is made using 25µL of this standard to 50mLof reagent water/Sample Matrix.

Stock Standard(ICV/LCS)	Conc (ng/µL)	Syringe(µL)	Amount(µL)	Final Conc (ng/µL)
2-CEVE(Vendor,Lot#)	20,000	25	20	200
Vinyl Acetate(Vendor,Lot#)	5000	100	80	200
Ketones(Vendor,Lot#)	5000	100	80	200
Liquid mix (Vendor,Lot#)	2000	100	100	100
Custom Mix(Vendor,Lot#)	5000	50	40	100
Gases (Vendor,Lot#)	2000	100	100	100
Acrolein/Acrylonitrile (Vendor,Lot#)	50,000	50	50	500

7.0 PROCEDURE

7.1 Chromatographic conditions – Refer to corresponding instrument maintenance log for current gas chromatograph, mass spectrometer, and concentrator conditions.

7.2 System Bakeout - Prior to analysis, the autosampler purge and trap unit is stepped to bake and an instrument blank is analyzed.

NOTE: Further cleaning may be accomplished by backflushing the lines with methanol and then analyzing blanks overnight.

7.3 Tuning - Prior to any calibration or analysis, BFB tuning criteria must be met for a 1.0µL injection of the tuning standard [see below]. Tune must be met every 12 hours sample analysis is to be performed (every 24 hours for *Federal Register* Method 624 except for South Carolina which only allows 12 hours). The mass spectrum of BFB is acquired as follows: by using one scan at the apex peak, or by using the mean of the apex and the preceding and following scans or mean of a symmetric pattern of scans about the apex, or using the average across the entire peak. Background subtraction is accomplished using a single scan no more than 20 scans prior to the elution of BFB.

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

7.4 Calibration: Calibration standards are made up in water using the appropriate amount of the methanol standard. Calibration for soils for South Carolina requires that 5mL of sodium bisulfate solution is added to each calibration standard made if the samples will be preserved with sodium bisulfate. All calibration standard integrations must be checked for acceptability.

7.4.1 Initial Calibration - An initial calibration curve at no less than five concentration levels must be analyzed and shown to meet the initial calibration criteria before any sample analysis may be performed. For Arizona samples the surrogates must also be calibrated at a minimum of five concentrations. Method 624 requires that the %RSD be less than 35% to use the average response factor for quantitation, the curve is to be used otherwise and should have a correlation coefficient (*r*) of $\geq$0.995. Method 8260B requires that the %RSD be less than 15% to use the average response factor for quantitation, the curve is to be used otherwise as long as ***r*** is $\geq$0.995. In addition, there are calibration check compounds (CCCs) listed below which must have a %RSD less than 30% and five system performance check compounds (SPCCs) which must meet the average response factor criteria listed below. The lowest standard must be less than or equal to the reported quantitation limit and the highest standard must not exceed the linear range of the detector. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram. Any response factors less than 0.050 must be supported by the mass spectrum of the lowest standard.

CCCs:	1,1-Dichloroethene	Toluene
	Chloroform	Ethylbenzene
	1,2-Dichloropropane	Vinyl chloride

SPCCs:	Chloromethane	0.10
	1,1-Dichloroethane	0.10
	Bromoform	0.10
	Chlorobenzene	0.30
	1,1,2,2-Tetrachloroethane	0.30

7.4.2 Initial Calibration Verification - A second source standard at the 50 µg/L (5mL purge) level is used to check the validity of the curve. The standard recovery for all analytes must be between 75 and 125%. If the second source recovery is above 125%, the main standard has probably deteriorated for that compound. That standard must be replaced and a new curve generated. If the second source recovery is below 75%, the second source standard has probably deteriorated for that compound and must be replaced. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram.

7.4.3 Continuing Calibration Verification (every 12 hours) - A midpoint calibration standard (generally 50 µg/L - 5mL purge) must be analyzed and calculated against the initial calibration curve, then shown to meet the calibration check criteria before any sample analysis may be performed. Acceptance criteria for method 8260B consists of the same SPCC criteria as

above and ≤20% drift or difference (calculations given in section 7.10) for the CCCs as listed above. The internal standards must also be evaluated as listed below. Any manual integrations are documented by inclusion of the integrated signals with the quantitation report and chromatogram. Samples are then quantitated against the initial calibration curve. Note: If any compound in the continuing calibration not subject to the criteria above exceeds 30% D, it must be evaluated and initialed by the organic section manager. If deemed acceptable, the analyst may continue analysis.
NOTE: Acceptance criteria for method 624 consists of meeting recovery limits found in table 5 for a QC check sample. This QC check sample is made from a separate source or lot number than the calibration standard at a concentration of 20 µg/L.

Internal standard checks

7.4.3.1.1 Retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.3.1.2 Response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 LCS - An LCS is analyzed every 12 hour tune. Using standards prepared from an alternate vendor or lot number, blank water is spiked at the 50 µg/L (5mL/soil) or 10 µg/L (25mL) level. See section 8.3 below for criteria and corrective action. Note: the concentration of the LCS will be 20 µg/L when analyzing 624 samples (QC Check Sample).

7.6 Method Blank - Prior to sample analysis, the system must be shown to be free of contamination through analysis of a method blank. See section 8.4 below for criteria and corrective action.

7.7 Sample Analysis - Prior to analysis, the samples are prepared for chromatography using the appropriate sample preparation method (5mL water, 25mL water, low soil, high soil, etc.) See SOP-225 for preparation of a 5035 soil sample. For a 5mL/25mL water sample, use the following procedure:

7.7.1. Load the vial into the Archon autosampler in the expected position.

7.7.2. Program the Archon for the loaded vial range and necessary dilutions, making sure the programmed method is set for the same volume as the purge vessel on the front of the LSC 2000 or 3100 and that the Chemstation sequence matches the Archon sequence. Note: TCLP samples are analyzed at a 10x dilution. One TCLP sample is spiked per matrix.

7.7.3. After analysis of the sample has been completed, check the pH of the sample using pH paper and verify it to be less than a pH of 2. If it is not, record the pH and generate a corrective action report. The sample report will have to be flagged for preservation if the analysis is being performed more than 7 days after sampling. [Note: TCLP samples do not require a pH check.]

7.8 Instrument sequence-The instrument sequence log is filled out prior to sample analyses.

An example of a typical instrument sequence log follows:
1-BFB Tune (12:00 am)
2-CCV
3-LCS
4-Method Blank
5-Sample
6-Sample
7-Sample
8-Sample
9-Sample
10-Sample
11-Sample
12-Sample
13-Sample
14-Sample
15-Sample
16-Sample
17-Sample MS
18-Sample MSD
19-BFB (12:00pm - 12 hours since last BFB/CCV)
20-CCV
21-LCS
22-Method Blank
23-Sample
24-Sample

7.9 Data Reduction/Evaluation - Each sample analysis sequence is documented using the computer run log generated on the chemstation. This run log is signed, dated and paginated then placed in a 3 ring binder for that instrument. After the sample has been analyzed, the data is processed through the TargetDB on Windows NT data system. Quantitative measurements are performed using the calculations found in section 7.9 below. The following must be checked to determine if the sample will need any reanalysis or dilution. Formal data evaluation is detailed in SOP-200

(documented using the USACE Analyst Data Review Checklist for USACE projects).

7.9.1 Internal Standards - Areas should be within 50 to 200 percent of the area of the continuing calibration. Retention time should be within 30 seconds of the retention time of the continuing calibration. Note: criteria applies to the continuing calibration, not samples, but is used as an indication of the sample analysis validity. If not, the sample and historical data should be evaluated to determine the cause of the problem. Reanalysis is expected if it appears to be from a leak. If matrix effect is confirmed by reanalysis or historical data, complete a corrective action report and flag the affected compounds on the final report for matrix effect.

7.9.2 Surrogates – Control limits are determined by charting LCSs and method blanks. All of the surrogates must be within these limits in order for the analysis to be in control. If not, the reason for the malfunction must be determined and reanalysis may be necessary. If historical data indicates matrix, the sample would be flagged appropriately. When the surrogates exceed either the control limits, a corrective action report must be completed. *Federal Register* Method 624 contains no criteria for surrogate recovery.

Surrogate	WATER	SOIL/SEDIMENT
Dibromofluoromethane	85-120	80-120
d4-1,2-Dichloroethane	85-130	75-135
d8-Toluene	85-115	85-115
Bromofluorobenzene	80-120	85-120

7.9.3 Analyte concentration must be within the range of the calibration curve after rounding to 2 significant figures. If an analyte exceeds the curve, a dilution must be performed, the next sample must be checked for carryover and the sparge position must be checked for contamination through the analysis of a system blank. Any dilution should keep the concentration of the analyte in question within the mid-range of the curve.

7.9.4 Qualitative identification is made as indicated below.

7.9.4.1 The mass spectra are compared to reference spectra in a user-created data base especially compiled to contain relatively uncontaminated mass spectra of each target compound. Note: Such a file cannot be obtained from the daily calibrations during each 12 hour analytical period due to overlapping peaks in the mixes.

7.9.4.2 The GC/MS analyst uses intelligence guided by experience to make the identifications. In uncontaminated spectra where ions are missing due to low concentration, if the major ions are present in the correct ratios at the correct retention time, the identification will be considered positive. In contaminated spectra, special emphasis will be placed upon higher mass ions, and the major ions will usually need to be present as major components of the spectrum (either unsubtracted or subtracted) for the identification to be positive. All

assessments of relative intensities of ions will be made by visual estimates from the spectra.

7.10 Calculations:

7.10.1 The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.

A_{is} = Peak area (or height) of the internal standard.

C_s = Concentration of the analyte or surrogate.

C_{is} = Concentration of the internal standard.

7.10.2 Calibration verification involves the calculation of the percent drift (linear) or the percent difference (average) of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference, depending on the calibration procedure used.

$$\% \text{ Drift} = \frac{(\text{Calculated concentration} - \text{Theoretical concentration}) * 100}{\text{Theoretical Concentration}}$$

where the calculated concentration is determined from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{(\text{CCV RF} - \text{Average RF}) * 100}{\text{Average RF}}$$

where CCV RF is the response factor from the analysis of the verification standard and Average RF is the average response factor from the initial calibration. The % difference or % drift calculated for the calibration verification standard must be within ±20% for each CCC analyte, or for all target analytes if the CCCs are not target analytes, before any sample analyses may take place.

7.10.3 Concentration in water samples is calculated as follows: [Note: Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to ug/L.]

$$\text{Concentration } (\mu g/L) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(V_s)(1000)}$$

where:

A_s = Area (or height) of the peak for the analyte in the sample.

A_{is} = Area (or height) of the peak for the internal standard.

C_{is} = Concentration of the internal standard in the volume purged in ug/L.

D = Dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.

V_i = For purge-and-trap analysis, V_i is not applicable and is set at 1.

$\overline{RF}$ = Mean response factor from the initial calibration.

V_s = Volume of the aqueous sample purged (mL). If units of liters are used for this term, multiply the results by 1000.

7.10.4 Concentration in non-aqueous samples is calculated as follows: [Note: Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to ug/kg.]

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(C_{is})(D)(V_i)}{(A_{is})(\overline{RF})(W_s)(1000)}$$

where: A_s,

A_{is}, C_{is}, D, and $\overline{RF}$ are the same as for aqueous samples, and

W_s = Weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

8.0 QUALITY ASSURANCE/QUALITY CONTROL/CORRECTIVE ACTIONS

8.1 Internals - All samples and QC are spiked with internals. See section 7.8.1 above for criteria and corrective action.

8.2 Surrogates - All samples and QC are spiked with surrogates. The surrogate recoveries from method blanks and LCS are used to generate control limits. See section 7.8.2 above for criteria and corrective action.

8.3 LCS Sample - An LCS is analyzed every 12 hour tune . To prepare the LCS, a blank is spiked with standards prepared from an alternate vendor or lot number from the calibration standards. Note: the concentration of the LCS will be 20 µg/L when analyzing 624 samples (QC Check Sample). The recoveries are used to generate control limits. See the LCS report forms in the appendix for the laboratory generated limits. The limits are in-house generated matrix spike limits or client specified limits for matrix spike analytes and 70-130% (or client specified limits) recovery for waters or soils for all other analytes if limits have not been generated. Limits for 624 LCSs are taken from table 5 of method 624. If the LCS compound has a recovery above the upper limit, but the same compound is not detected in any of the batch samples, no corrective action is required. For all other situations, the LCS should be reanalyzed for the failed analytes only. If the second analysis fails, all associated samples should be reanalyzed for the failed analytes only.

8.4 Method Blanks - The concentration for most method target analytes must be < ½ the reporting limit. Common laboratory contaminants, such as acetone and methylene chloride, must be < the reporting limit. The first step of corrective action is to assess the affect on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps should be taken to find/reduce/eliminate the source of this contamination in the method blank. If an analyte is found in the method blank and some, or all, of the other batch samples, then corrective action is required. The source of contamination must be investigated and appropriate action taken and documented to find/reduce/eliminate the source of this contamination. The method blank, and any samples containing the same contaminant, would likely be reanalyzed. For the common laboratory contaminants, meeting the above requirements is not practical. Random cases of contamination are difficult to control, however, daily contamination is not acceptable and corrective action is essential. If a contaminant is found in the method blank and the samples, the compound concentration must be flagged with a 'B' on the final report unless the concentration is greater than 10x that found in the method blank. A method blank is analyzed every 12 hour tune.

8.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample - 1 in 20 samples are spiked for an MS/MSD with the LCS standard. Criteria for the MS/MSD recoveries are the same as the LCS limits. Limits for the RPDs are found on the forms in the appendix. Samples that do not meet these criteria due to matrix must be flagged on the final report for QC problems. Generally, batch control is not based on MS/MSD results unless general method failure is determined to be the problem. In that case, the samples and associated QC would be reanalyzed for the failed analytes only. MS data evaluation must include the consideration of the following factors.

8.5.1 Sample matrix - If the sample is a soil, grab sample or sequentially collected water sample it may affect the %R and RPD of the MS/MSD. A water sample which was taken from the same VOA vial for the original sample and the MS/MSD should have very good RPDs unless there has been a method problem. Corrective action must be taken in the form of reanalysis if a method problem is indicated.

8.5.2 Original sample concentration - If a spiked compound has a problem and the concentration of that compound in the original sample was two or more times the concentration of the spike, no further corrective action may be necessary other than the generation of a corrective action report to document the problem.

8.5.3 MS vs. MSD - If a spiked compound has a problem in both the MS and MSD, review the LCS and if acceptable no further action may be necessary since it is attributable to matrix effect.

8.5.4 Non-target Interference - The presence of significant non-target interference should be brought to the immediate attention of your supervisor who should discuss the problem with the client/project manager to determine the action to be taken.

9.0 HEALTH AND SAFETY

9.1 Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of blue nitrile gloves and lab coats is highly recommended.

9.2 Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples that need special consideration have applicable notes on the sample logs.

9.3 MSDS sheets are available for all reagents and standards that have been purchased. These are located in the office next to the technical director.

10. WASTE MANAGEMENT AND POLLUTION PREVENTION

10.1 Please see Waste Disposal, SOP-210 and SOP-405 for proper disposal of waste coming from this area within our laboratory.

10.2 Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

11.0 EXAMPLE FORMS

Definitions and examples of the instrument run log, LCS report sheets (624, water and soil) and the USACE analyst data review checklist are located in the following Appendix.

APPENDIX

TABLE OF DEFINITIONS

1. amu- atomic mass unit
2. BFB- Bromofluorobenzene
3. °C- degrees Centigrade
4. CCC- Calibration Check Compound
5. CCV- Continuing Calibration Verification
6. CLP- Contract Laboratory Program
7. %D- percent difference
8. EICP- extracted ion current profile
9. EPA- Environmental Protection Agency
10. g- gram or grams
11. GC- Gas Chromatograph
12. GC/MS- Gas Chromatograph/Mass Spectrometer
13. ICV- Initial Calibration Verification
14. I.D.- inner diameter
15. ISTD- internal standard
16. LSC- Laboratory Sample Concentrator
17. MDL- method detection limit
18. MS- Matrix Spike
19. MSD- Matrix Spike Duplicate
20. M.S.- Mass Spectrometer
21. µm- micometer
22. µL- microliter
23. mL- milliliter
24. mm- millimeter
25. ng- nanogram
26. P&T- purge and trap
27. QC- quality control
28. %R- percent recovery
29. RPD- relative percent difference
30. %RSD- percent relative standard deviation
31. SOP- Standard Operating Procedure
32. Surr.- surrogate
33. SPCC- System Performance Check Compound
34. TCLP- Toxicity Characteristic Leaching Procedure
35. USACE- United States Army Corps Of Engineers
36. VOA- volatile organic analysis
37. LCS- Lab Control Sample

REFERENCES

1. *40 CFR, Part 136*; Appendix A
2. *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition
3. *National Environmental Laboratory Accreditation Conference*; CH. 5, 2001
4. USACE, *EM 200-1-3; Appendix 1; Shell*, 2/2001
5. *DOD Quality Systems Manual for Environmental Laboratories*, 6/2002

FORM 3

WATER VOLATILE LAB CONTROL SAMPLE (624)

Lab Name: Empirical Laboratories, LLC Contract: ELAB

Lab Code: NA Batch No.: NA SAS No.: NA SDG No.:

Matrix Spike - Client Sample No.:

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONCENTRATION (ug/L)	LCS CONCENTRATION (ug/L)	LCS % REC #	QC. LIMITS REC.
Acrolein	100.00	0.0000	100.000	100	NML
Acrylonitrile	100.00	0.0000	100.000	100	NML
Benzene	20.00	0.0000	20.000	100	37-151
Bromodichloromethane	20.00	0.0000	20.000	100	35-155
Bromoform	20.00	0.0000	20.000	100	45-169
Bromomethane	20.00	0.0000	20.000	100	D-242
Carbon tetrachloride	20.00	0.0000	20.000	100	70-140
Chlorobenzene	20.00	0.0000	20.000	100	37-160
Chloroethane	20.00	0.0000	20.000	100	14-230
2-Chloroethyl vinyl eth	40.00	0.0000	40.000	100	D-305
Chloroform	20.00	0.0000	20.000	100	51-138
Chloromethane	20.00	0.0000	20.000	100	D-273
Dibromochloromethane	20.00	0.0000	20.000	100	53-149
1,2-Dichlorobenzene	20.00	0.0000	20.000	100	18-190
1,3-Dichlorobenzene	20.00	0.0000	20.000	100	59-156
1,4-Dichlorobenzene	20.00	0.0000	20.000	100	18-190
1,1-Dichloroethane	20.00	0.0000	20.000	100	59-155
1,2-Dichloroethane	20.00	0.0000	20.000	100	49-155
1,1-Dichloroethene	20.00	0.0000	20.000	100	D-234
trans-1,2-Dichloroethen	20.00	0.0000	20.000	100	54-156
1,2-Dichloropropane	20.00	0.0000	20.000	100	D-210
cis-1,3-Dichloropropene	20.00	0.0000	20.000	100	D-227
trans-1,3-Dichloroprope	20.00	0.0000	20.000	100	17-183
Ethylbenzene	20.00	0.0000	20.000	100	37-162
Methylene chloride	20.00	0.0000	20.000	100	D-221
1,1,2,2-Tetrachloroetha	20.00	0.0000	20.000	100	46-157
Tetrachloroethene	20.00	0.0000	20.000	100	64-148
Toluene	20.00	0.0000	20.000	100	47-150
1,1,1-Trichloroethane	20.00	0.0000	20.000	100	52-162
1,1,2-Trichloroethane	20.00	0.0000	20.000	100	52-150
Trichloroethene	20.00	0.0000	20.000	100	71-157
Trichlorofluoromethane	20.00	0.0000	20.000	100	17-181
Vinyl chloride	20.00	0.0000	20.000	100	D-251

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

NML = No Method Limits

COMMENTS: _____

_____

VOA Water Limits

	Water	DOD Limits		Final
1,1,1 Trichloroethane	80-130	65-130		80-130
1,1,1,2-Tetrachlorethane	85-120	80-130		85-120
1,1,2,2-Tetrachloroethane	55-140	65-130		65-130
1,1,2-Trichloroethane	80-120	75-125		80-120
1,1-Dichloroethane	80-125	70-135		80-125
1,1-Dichloroethene	65-120	70-130		70-130
1,2,4 Trichlorobenzene	60-125	65-135		65-135
1,2-Dibromo-3-chloropropane	65-125	50-130		65-125
1,2-Dibromoethane	85-115	80-120		85-115
1,2-Dichlorobenzene	85-110	70-120		85-110
1,2-Dichloroethane	75-130	70-130		75-130
1,2-Dichloropropane	80-120	75-125		80-120
1,3-Dichlorobenzene	80-110	75-125		80-110
1,4-Dichlorobenzene	80-110	75-125		80-110
2-Butanone	65-140	30-150		65-140
2-Hexanone	75-140	55-130		75-140
4-Methyl-2-pentanone	75-135	60-135		75-135
Acetone	65-155	40-140		70-130
Benzene	75-120	80-120		80-120
Bromochloromethane	85-120	65-130		85-120
Bromodichloromethane	85-140	75-130		85-140
Bromoform	70-130	70-130		70-130
Bromomethane	50-160	30-145		50-160
Carbon disulfide	65-145	35-160		65-145
Carbon tetrachloride	75-135	65-140		75-135
Chlorobenzene	80-110	80-120		80-110
Chloroethane	60-145	60-135		60-145
Chloroform	80-125	65-135		80-125
Chloromethane	35-160	40-125		40-125
Cis-1,2-Dichloroethene	75-125	70-125		75-125
Cis-1,3-Dichloropropene	80-125	70-130		80-125
Dibromochloromethane	80-120	60-135		80-120
Dibromomethane	90-120	75-125		75-125
Dichlorodifluoromethane	10-180	30-155		30-155
Ethylbenzene	80-120	75-125		80-120
Methylene chloride	65-135	55-140		70-130
M,p-Xylene	80-120	75-130		80-120
o-Xylene	80-120	80-120		80-120
Styrene	80-120	65-135		80-120
Tetrachloroethene	75-115	45-150		75-115
Toluene	75-115	75-120		75-115
Trans-1-2 Dichlorethene	75-125	60-140		75-125
Trans-1-3-Dichloropropene	75-115	55-140		75-115
Trichloroethene	75-120	70-125		75-120
Trichloroflurormethane	70-140	60-145		70-140
Vinyl chloride	40-150	50-145		50-145

VOA Soil Limits

	Soil	DOD Limits		Final
1-1-1-2 Tetrachloroethane	75-130	75-125		75-130
1-1-1-Trichloroethane	75-130	70-135		75-130
1-1-2-2-Tetrachloroethane	65-130	55-130		65-130
1-1-2-Trichloroethane	70-130	60-125		70-130
1-1-Dichloroethane	75-130	75-125		75-130
1-1-Dichloroethene	65-115	65-135		65-115
1-2-4-Trichlorobenzene	65-125	65-130		65-125
1-2-Dibromo-3-chloropropane	60-135	40-135		60-135
1-2-Dibromoethane	75-125	70-125		75-125
1-2-Dichlorobenzene	75-120	75-120		75-120
1-2-Dichloroethane	75-135	70-135		75-135
1-2-Dichloropropane	75-120	70-120		75-120
1-3-Dichlorobenzene	70-120	70-125		70-120
1-4-Dichlorobenzene	60-135	70-125		70-125
2-Butanone	60-145	30-160		60-145
2-Hexanone	60-140	45-145		60-140
4-Methyl-2-pentanone	70-135	45-145		70-135
Acetone	30-180	20-160		70-130
Benzene	75-115	75-125		75-115
Bromochloromethane	80-120	70-125		80-120
Bromodichloromethane	85-140	70-130		85-140
Bromoform	70-125	55-135		70-125
Bromomethane	45-170	30-160		45-170
Carbon disulfide	65-145	45-160		65-145
Carbon tetrachloride	75-125	65-135		75-125
Chlorobenzene	75-120	75-125		75-120
Chloroethane	55-145	40-155		55-145
Chloroform	75-125	70-125		75-125
Chloromethane	40-155	50-130		50-130
Dibromochloromethane	70-125	65-130		70-125
Dibromomethane	80-120	75-130		80-120
Dichlorodifluoromethane	15-150	35-135		35-135
Ethylbenzene	70-120	75-125		70-120
Methylene chloride	35-170	55-140		70-130
Styrene	70-120	75-125		70-120
Tetrachloroethene	65-125	65-140		65-125
Toluene	70-120	70-125		70-120
Trichloroethene	75-120	75-125		75-120
Trichlorofluoromethane	65-130	25-185		65-130
Vinyl Acetate	10-240			10-240
Vinyl chloride	40-140	60-125		60-125
cis-1-2-Dichlorethene	75-120	65-125		75-120
cis-1-3-Dichloropropene	80-130	70-125		80-130
m-p-Xylene	70-120	80-125		70-120
o-Xylene	70-120	75-125		70-120
trans-1-2-Dichloroethene	75-120	65-135		75-120
trans-1-3--Dichloropropene	65-120	65-125		65-120

VOA MIXES

LIQUID MIX (2000PPM)
C-610H (PRIMARY STANDARD)
M-502A-R-10X (ICV/LCS/MATRIX SPIKE)

Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
n-Butylbenzene
sec-Butylbenzene
tert-butylbenzene
Carbon tetrachloride
Chlorobenzene
Chloroform
2- & 4-Chlorotoluene
Trichloroethene
Dibromochloromethane
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,1- & 1,2-Dichloroethane
1,1,2-Trichloroethene
1,1-Dichloroethene
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2- & 1,3-Dichloropropane
1,2,3-Trichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethylbenzene
Hexachlorobutadiene
Isopropylbenzene
Isopropyltoluene
Methylene Chloride
Naphthalene
n-Propylbenzene
Styrene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
1,2,3-Trichlorobenzene
1,2,3-Trimethylbenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
m-,p- & o-Xylene
1,1,1-Trichloroethene

GASES MIX (2000PPM)
#30042 (PRIMARY STANDARD)
M-502B-R-10X (ICV/LCS/MATRIX SPIKE)

Bromomethane
Chloroethane
Vinyl chloride
Chloromethane
Dichlorodifluoromethane
Trichlorofluoromethane

C610H-PRIMARY STANDARD
M60310X (ICV/LCS/MATRIX SPIKE)

Acrolein (10,000PPM)
Acrylonitrile (10,000PPM)

CCS1037-PRIMARY CUSTOM MIX (5000PPM)
#557102- ICV/LCS CUSTOM MIX (5000PPM)

Tetrahydrofuran
MTBE
Methyl metacrylate
Ethyl methacrylate
1,1,2-Trichlorotrifluoroethane
Cyclohexane
Methylcyclohexane
Methyl acetate
Carbon disulfide
Iodomethane

PRIMARY and ICV/LCS STANDARD-neat

Vinyl acetate (5000PPM)

PRIMARYand ICV/LCS STANDARD-neat

2-Chloroethyl vinyl ether (20000PPM)

KETONES MIX (5000PPM)
#30006 (PRIMARY STANDARD and ICV/LCS) different lots

Acetone
2-butanone
2-hexanone
4-methyl-2-pentanone

VOA CALIBRATIONS RANGE FOR EPA8260B/624(AQUEOUS)

Liquid mix, Gases mix & primary custom mix is calibrated at these levels - 0.5ppb, 1.0ppb, 2.0ppb, 10ppb, 20ppb, 50ppb, 100ppb & 200ppb. The ketones mix, 2-chloroethyl vinyl ether & vinyl acetate are calibrated at these levels - 1.0ppb, 2.0ppb, 4.0ppb, 20ppb, 40ppb, 100ppb, 200ppb & 400ppb. Acrolein & Acrylonitrile are calibrated at these levels – 2.5ppb, 5.0ppb, 10ppb, 50ppb, 100ppb, 250ppb, 500ppb, 1000ppb.

VOA CALIBRATIONS RANGE FOR EPA8260B(SOLIDS)

Liquid mix, Gases mix & primary custom mix is calibrated at these levels – 2.0ppb, 5.0ppb, 10ppb, 20ppb, 50ppb, 100ppb & 200ppb. The ketones mix, 2-chloroethyl vinyl ether & vinyl acetate are calibrated at these levels - 2.0ppb, 10ppb, 20ppb, 40ppb, 100ppb, 200ppb & 400ppb. Acrolein & Acrylonitrile are calibrated at these levels – 5.0ppb, 10ppb, 50ppb, 100ppb, 250ppb, 500ppb, 1000ppb.

VOA LCS/ICV/MATRIX SPIKE LEVEL FOR EPA8260B

Liquid mix, Gases mix, Ethyl methacrlate, Metyl methacrylate, Tetrahydrofuran, MTBE, Trichlorotrifluoroethane, Cyclohexane, Methylcyclohexane & Methyl acetate are spiked at 50ppb level. Acrolein & Acrylonitrile spiked at 250ppb level. Acetone, 2-Butanone, 2-Hexanone, Carbon disulfide, 2-Chloroethyl vinyl ether, 4-Methyl-2-pentanone, Vinyl acetate & Iodomethane are spiked at 100ppb level.

INTERNAL STANDARD ASSOCIATION / QUANT ION TABLE

COMPOUND	QUANT MASS	* I.S.	COMPOUND	QUANT MASS	* I.S.
			Dibromomethane	93	1
*Fluorobenzene (1)	96		1,1,2-Trichloroethane	83	2
*Chlorobenzene-d5 (2)	117		1,2,3-Trichloropropane	110	2
*1,4-Dichlorobenzene-d4 (3)	152		Hexachlorobutadiene	225	3
			Isopropylbenzene	105	2
Bromomethane	94	1	Isopropyltoluene	119	3
Chloroethane	64	1	Methylene Chloride	84	1
Vinyl chloride	62	1	Naphthalene	128	3
Chloromethane	50	1	Propionitrile	54	1
Dichlorodifluoromethane	85	1	n-Propylbenzene	91	3
Acetonitrile	41	1	Styrene	104	2
Allyl chloride	41	1	1,1,1,2-Tetrachloroethane	131	2
Trichlorofluoromethane	101	1	1,1,2,2-Tetrachloroethane	83	3
Benzene	78	1	Tetrachloroethene	166	2
Bromobenzene	156	3	Toluene	92	2
Bromochloromethane	128	1	1,2,3-Trichlorobenzene	180	3
Bromodichloromethane	83	2	1,2,4-Trichlorobenzene	180	3
Bromoform	173	2	1,2,4-Trimethylbenzene	105	3
n-Butylbenzene	91	3	1,3,5-Trimethylbenzene	105	3
sec-Butylbenzene	105	3	m-Xylene	91	2
tert-butylbenzene	119	3	p-Xylene	91	2
Carbon tetrachloride	117	1	o-Xylene	91	2
Chlorobenzene	112	2	Acrolein	56	1
Chloroform	83	1	Acrylonitrile	53	1
Chloroprene	53	1	Tetrahydrofuran	42	1
2-Chlorotoluene	91	3	MTBE	73	1
4-Chlorotoluene	91	3	Methacrylonitrile	41	1
Dibromochloromethane	129	2	Methyl methacrylate	41	1
1,2-Dibromo-3-chloropropane	157	3	Ethyl methacrylate	69	2
1,2-Dibromoethane	107	2	1,1,2-Trichlorotrifluoroethane	101	1
1,2-Dichlorobenzene	146	3	Cyclohexane	56	1
1,3-Dichlorobenzene	146	3	Methylcyclohexane	83	1
1,4-Dichlorobenzene	146	3	Methyl acetate	43	1
1,1-Dichloroethane	63	1	Carbon disulfide	76	1
1,2-Dichloroethane	62	1	Iodomethane	142	1
1,1-Dichloroethene	96	1	Vinyl acetate	43	1
cis-1,2-Dichloroethene	96	1	2-Chloroethyl vinyl ether	63	1
trans-1,2-Dichloroethene	96	1	Acetone	43	1
trans-1,4-Dichloro-2-butene	53	3	2-butanone	43	1
1,2-Dichloropropane	63	1	2-hexanone	43	2
1,3-Dichloropropane	76	2	Isobutyl alcohol	43	1
2,2-Dichloropropane	77	1	1,4-Dioxane	88	1
1,1-Dichloropropene	75	1	4-methyl-2-pentanone	43	1
cis-1,3-Dichloropropene	75	1	Dibromofluoromethane (S)	111	1
trans-1,3-Dichloropropene	75	2	1,2-Dichloroethane-d4 (S)	102	1
Ethylbenzene	91	2	Toluene-d8 (S)	98	2
1,1,1-Trichloroethane	97	1	Bromofluorobenzene (S)	95	2
Trichloroethene	95	1			

***I.S=internal Standard.**
S=surrogate.

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):	
Batch Number(s):	
Method:	**8260B/8270C (Circle One)**

QA/QC Item	Yes	No	NA	Second Level Review
1. Is the BFB/DFTPP tune performed every 12 hours and is the tuning criteria met?				
2. Are the RRFs and % RSDs within QC limits for appropriate analytes for the initial calibration? Check the retention times for compounds with the same spectra. Check compounds with different conc.(eg. m/p-xylene, ketones,etc.).				
3. Was the initial calibration curve verified by a second source calibration standard (ICV) and have criteria been met?				
4. Does the Continuing Calibration Standard (CCV) meet the criteria for the CCCs and SPCCs.				
5. Is the Method Blank run at the desired frequency and is its concentration for target analytes less than the MDLs?				
6. Are the LCS, MS, MSD within control limits and run at the desired frequency?				
7. Are all sample holding times met, analytes within calibration range, IS areas and surrogate recoveries within QC limits?				
8. Was the Method Blank, LCS, MS, MSD and samples loaded to the GCMS_LFSYS Tablespace within the Target DB Database?				

Comments on any "No" response:

Primary-Level Review: _____ Date: _____

Second-Level Review: _____ Date: _____

GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD)

ORGANOCHLORINE PESTICIDES/POLYCHLORINATED BIPHENYLS (PCB) BY

EPA METHOD 608/608.2 AND

SW846 METHOD 8081A/8082

SOP NUMBER: SOP-211

REVISION NUMBER: 17

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: 10/04/06

Date of Last Review: 10/04/06

GAS CHROMATOGRAPHY/ELECTRON CAPTURE DETECTOR (GC/ECD) ORGANOCHLORINE PESTICIDES/POLYCHLORINATED BIPHENYLS (PCB) BY EPA METHOD 608/608.2 AND SW-846 METHOD 8081A/8082

1.0 SCOPE AND APPLICATION

This Standard Operating Procedure, SOP, (based primarily on SW-846 Methods 8000B/8081A/8082) is used for the analysis of Pesticide/PCB organic compounds in a variety of matrices (soils, sediments, waters, etc.). Methods SW-846 8082, *Federal Register* Method 608/608.2 and CLP Method for Pesticides have also been used in the development of this SOP. The analyses by these various methods are clearly defined in the respective regulatory manuals. A good understanding of these different methods is essential to the performance of each method. The normal laboratory list of analytes with their LCS limits is found attached in the appendix. Other compounds may be analyzed by this SOP as detailed in section 1.0 of SW-846 Methods 8081A/8082. Any questions left by this SOP should be answered by reading the methods, paying close attention to SW-846 8000B/8081A/8082, EPA 608/608.2 and CLP. If questions still remain unanswered, check with the Organic Lab Manager, Quality Assurance Officer and/or Technical Director.

2.0 METHOD SUMMARY

After sample preparation using the appropriate extraction technique, the sample is introduced into the GC using direct injection. The analytes are separated in the gas chromatograph by a combination of the temperature program and the capillary column. The analytes are then detected by the ECD. Pesticide analytes are identified and confirmed based on the retention time of known standards. PCB and multi-component pesticide analytes are identified based on pattern recognition. Analytes are quantitated relative to known standards using the external standard method.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Section 7.0 and tables 6-1 and 6-2 of the Empirical Laboratories, LLC Quality Assurance Manual includes details concerning sample preservation, containers and handling of samples and extracts. All water and soil samples are stored in the appropriate walk-in cooler in sample storage at a temperature of 1°C – 4.4°C. All extracts are stored in the Hobart in the Extraction laboratory at a temperature of 1°C – 4.4°C. Water samples have a holding time of 7 days from date of sampling to extraction. Soil samples have a holding time of 14 days from date of sampling to extraction (unless otherwise specified for the project). Extracts have a holding time of 40 days from extraction to analysis.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Section 3.0 of SW-846 Methods 8081A/8082 details interferences and potential problems which may be encountered when dealing with pesticide/PCB analyses. Please see sample clean-up SOPs (307, 308, 309, 330, and 334) to evaluate possible clean-up options for any encountered interferences.

5.0. EQUIPMENT AND APPARATUS

5.1 GC's:

5.1.1 HP 5890- complete with temperature programmable gas chromatograph suitable for split/splitless injection.

5.1.2 Agilent 6890N- complete with temperature programmable gas chromatograph suitable for split/splitless injection.

5.2 Columns:

5.2.1 RTX-CLP (or equivalent): 30 meter x 0.32 mm ID x 0.5 µm film thickness fused silica column.

5.2.2 RTX-CLP II (or equivalent): 30 meters x 0.32 mm ID x 0.5 µm film thickness fused silica column.

5.3 Autosamplers:

5.3.1 HP 7673A/HP7673 autosamplers capable of reproducibility from one injection to another, proven by meeting QC and calibration criteria.

5.3.2 Agilent 7683 autosamplers capable of reproducibility from one injection to another, proven by meeting QC and calibration criteria.

5.4 Acquisition Software: HP Chemstation system is interfaced to the GC. The system acquires and stores data throughout the chromatographic program.

5.5 Data Processing Software: Target DB Windows NT data system is interfaced to the HP Chemstation. The system accepts, processes and stores acquired data.

6.0 REAGENTS

6.1 Hexane - pesticide quality or equivalent.

6.2 Stock standards are purchased in mixtures from reputable vendors. The date they are received is noted on the label and recorded in the GC standards logbook. The date they are opened is noted on the label and recorded in the GC standards logbook along with their lot number and vendor and given a sequential number. Each standard that is prepared is recorded in the GC standards logbook and given a sequential number. The following are noted in the logbook: standard makeup, solvent used, date received, date opened, date prepared, expiration date and analyst. Each standard label is completed with the standard number, name, preparation date, expiration date, solvent and analyst initials. All stocks and standards are stored in the refrigerator at a temperature of 1°C-4.4°C from the date they are received/prepared. The refrigerator and freezer temperature is monitored daily with an annually calibrated thermometer and recorded with calibration correction in the GC refrigerator temperature logbook. See the GC standards log book for makeup of intermediate and calibration standards.

6.2.1 The Initial Calibration Verification (ICV) intermediate standard is prepared from the vendor stock standards in the same manner as the Calibration intermediate standards above and is stored in the refrigerator at a temperature of 1°C-4.4°C for up to 6 months. The ICV standard is then prepared at a concentration near the midpoint in the same manner as the Calibration standards above.

7.0 PROCEDURE

The GC/ECD should be primed by injecting a pesticide standard at 100 µg/L and/or PCB standard at 10,000 µg/L, 10 times more concentrated than the mid-level standard. Inject this prior to beginning initial or daily calibration.

7.1 Chromatographic conditions:

7.1.1 RTX-CLP/RTX CLPII columns:

GC	ECD1/ECD3
Purge on	0.50 min.
Injector/Detector temperature	200/310°C
Column flow	@1.9 mL/min
Initial column temperature	130°C for 1.0 minutes
Temperature ramp	10°C/min
Final column temperature	310°C for 5.0 minutes

7.1.2 DB-XLB/DB-35MS columns:

GC	ECD4
Purge on	0.50 min.
Injector/Detector temperature	200/330°C
Column flow	@2.4 mL/min
Initial column temperature	110°C for 0.5 minutes
Temperature ramp	15°C/min
Final column temperature	320°C for 10 minutes

7.2 Eval Mix – Before pesticide calibration and/or sample analysis, a degradation check standard (evaluation mix) of endrin and 4,4-DDT must be injected. Degradation of either compound must not exceed 15 percent. If 15 percent degradation is exceeded, then corrective action must be taken (GC system maintenance, see SOP-222).

7.3 Calibration - (See SW-846 Method 8000B Section 7.4.2).

7.3.1 Initial Calibration – For single component pesticides and surrogates, a six point calibration is injected and analyzed for each analyte of interest. For Toxaphene and Technical Chlordane a single point standard is analyzed unless they are expected then a five point calibration is injected and analyzed. Injection volume for standards and samples is equal to 2 µL using the same injection technique to introduce both standards and samples (use of auto-injectors makes this a constant). All calibration integrations must be evaluated and any manual integrations are documented by the inclusion of the chromatogram (which includes peak integrations) with the quantitation report. The percent relative standard deviation (RSD) of the calibration factor must be <20% over the working range for each analyte of interest. When the 20% criteria is exceeded for an analyte, a linear calibration may be used if the correlation coefficient (r) is ≥0.995, ≥0.99 for quadratic with 6 points. Otherwise, a new standard curve should be prepared for each analyte that exceeded the criteria.

Initial calibration for Aroclors may be accomplished by using a six-point curve that contains Aroclors 1016 and 1260. The mixture of these two Aroclors contains many of the peaks represented in the other five Aroclor mixtures(1221, 1232, 1242, 1248 & 1254).

The curves for Aroclors 1016 and 1260 are used to show the linearity of the detector and can be used to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. The 1016/1260 curve may also be used to quantitate any 1016 or 1260 hits that may be seen in the samples. The analyst has the choice of running a curve for the other five Aroclor mixtures or when the calibration factor for the curve for 1016/1260 is <20% a single point calibration at the midpoint level concentration can be used for the other Aroclors. The injection procedure for Aroclors is the same as single component pesticides. The percent relative standard deviation (RSD) of the calibration factor must be <20% but this applies to the average of the quantitation peaks. When the 20% criteria is exceeded for an analyte, a linear calibration may be used if the correlation coefficient factor (r) is ≥0.995, ≥0.99 for quadratic with 6 points. Otherwise, a new standard curve should be prepared for each analyte that exceeded the criteria.

7.3.2 Initial Calibration Verification - A second source standard at the midpoint level is used to check the validity of the curve. The standard recovery for all analytes must be between 85 and 115%(**80-120% DOD QSM Ver.3**). If the second source recovery is above 115%, it is possible that the main standard has deteriorated for that compound. That standard should be remade and reevaluated. If that does not correct the problem, the standard should probably be replaced and a new curve generated. If the second source recovery is below 85%, the second source standard may have deteriorated for that compound. This standard should be remade and reanalyzed. If this does not correct the problem, the standard should be replaced. All calibration integrations must be evaluated and any manual integrations are documented by the inclusion of the chromatogram (which includes peak integrations) with the quantitation report.

7.3.3 Continuing Calibration Verification (CCV) - A mid-level standard must be analyzed every 12 hours (not to exceed 20 samples and cannot exceed 15 percent difference (%D), (**at the beginning and end of sequence and after every 10 field samples, 20%D no average DOD QSM Ver.3**) from the average calibration factor of the calibration curve. A CCV must also be analyzed at the end of the analysis sequence. If a CCV fails, GC maintenance may be necessary (see SOP-222), reanalysis may be required (for samples analyzed since the last valid CCV) and a corrective action report must be completed. If none of the failed target compounds exceed 30% D and the average of all the %Ds are < 15% then the CCV may be used without any further corrective action. Alternatively, analytes may be flagged depending on their concentration and the status of the analyte in the mid-level standard. No reanalysis is necessary if the analyte is undetected in the samples and recovered high in the CCV. All calibration integrations must be evaluated and any manual integrations are documented by the inclusion of the chromatogram (which includes peak integrations) with the quantitation report. Samples are then quantitated against the initial calibration curve.

7.4 RT Windows - Retention time criteria set forth in SW-846 method 8000B section 7.6 are used to set retention time windows. New in-house retention time windows are established after every major change to the system (new column or temperature program) and at initial calibration using

the midpoint standard RTs. If the established retention time window is less than +/-0.03 minutes, the window defaults to +/-0.03 minutes. Retention times are updated with the first CCV of the day or the mid-level standard of the curve if samples are analyzed directly after a curve.

7.5 Laboratory Control Sample (LCS) - The LCS is extracted 1 per extraction batch of up to 20 samples. The LCS is spiked with standards prepared from an alternate vendor or lot number than the calibration standards. See section 8.2 below for criteria and corrective action.

7.6 Method Blank - Method blanks are extracted at a minimum of 1 per extraction batch – up to 20 samples. See section 9.3 below for criteria and corrective action.

7.7 Samples - Prior to using Method 608, SW-846 8081A/8082, or CLP (pesticide method) the samples are prepared for chromatography using the appropriate sample preparation and clean up methods (generally SW-846 methods 3510, 3520, 3540, 3640, 3550, 3580, EPA method 608 or CLP).

7.7.1 Example of a sequence run log:

1-Primer A/B Mix-1000 or Primer PCB-10,000
2- EVAL Mix (Pest only)
3- CCV A/B Mix
4- CCV Toxaphene (single point)
5-CCV Chlordane (single point)
6- CCV PCB 1660
7- Method Blank
8-LCS A/B Mix
9-LCS PCB
10-Sample
11-Sample
12-Sample
13-Sample

14-Sample
15-Sample
16-Sample
17-Sample
18-Sample
19-Sample
20-Sample
21-Sample-MS
22-Sample-MSD
23-Sample
24-Sample
25-Sample
26-Sample
27-Sample
28-Sample
29- CCV A/B Mix
30-CCV PCB

7.8 Data Reduction/Evaluation - Each sample analysis sequence is documented in the run logbook for the instrument. After the sample has been analyzed, the data is processed through the Target DB Windows NT data system. Quantitative measurements are performed as described in SW-846 8081A section 7.5.6. Rounding is performed using CLP odd/even rounding rules. The following must be checked to determine if the sample will need any reanalysis, cleaning or dilution. Formal data evaluation is detailed in SOP-216 (documented using the USACE Analyst Data Review Checklist for USACE projects).

7.8.1 Analyte concentration after rounding to 2 significant figures must be within the range of the calibration curve. If an analyte exceeds the curve, a dilution must be performed and the next sample must be checked for carryover. Any dilution should keep the concentration of the analyte in question within the mid-range to the top half of the curve.

7.8.2 If the sample shows signs of sulfur contamination in the time range where sulfur compounds elute a sulfur cleanup is required [see SOP-307].

7.8.3 If the sample has extraneous peaks eluting in the chromatogram an acid cleanup is required for PCB samples and may be applicable for certain pesticides, (acid clean-up may be required for all PCB samples, check with your supervisor), [see SOP-308].

7.8.4 If the sample has extraneous peaks that are not removed by acid (PCB samples) and is not a sulfur interference, a florisil cleanup is recommended [see SOP-309]. A silica cleanup may also be used [see SOP-331].

7.8.5 Surrogates – Control and warning limits are determined by using all blank spikes in the calculation, (LCSs and method blanks). All limits used are generated in-house or client specified (with the exception that if the in-house limit's highest lower limit would be 90 and the lowest upper limit would be 110 examples: **98**-120 would be **90**-120 or 45-**75** would be 45-**110**). Surrogate standard recovery must be checked to determine if it is within these limits. Two surrogates are added to each sample for pesticides. Only one surrogate, DCB, is added to each PCB sample. Corrective action should be evaluated when any surrogate(s) is outside the action limits for a sample. When only one surrogate for pesticides exceed control limits on the primary and/or confirmation column corrective action may not be required. If both surrogates for pesticides (or DCB for PCB analyses) exceed control limits on the primary and/or confirmation column corrective action is required. A corrective action form should be filled out and given to the organic lab manager when both surrogates for pesticides (or DCB for PCB analyses) are outside the action or warning limits. The organic lab manager will then make suggestions as to what action should be taken, for example: the sample may need to be reanalyzed, reextracted, or flagged on the report for a QC problem. **DOD limits will be used for DOD QSM Ver. 3 projects.**

	WATER	SOIL/SEDIMENT	WIPES
Surrogate	In-House	In-House	In-House
TCMX	25-120	30-120	80-143

DCB	25-130	35-140	73-142

7.9 Identification/Quantitation [See SW-846 method 8081A section 7.6 or method 8082 sections 7.7-7.9].

7.9.1 Single peak components are identified by retention time on a primary column with confirmation by retention time on a secondary or confirmation column. Which column is used for primary/confirmation is determined by the chromatography in the region of the compound. The control limit for percent difference (%D) of compounds that confirmed from the primary column on the confirmation column is 40%. If both columns are equivalent, the highest concentration is reported.

7.9.1.1 Due to coelution of certain compounds confirmation for all analytes may not be achieved. The analyst must use experience and judgment to decide if the compound is there. If a call is made, the data should be flagged appropriately.

7.9.1.2 If a compound is outside of it's window on one column but in the window on the other column, the analyst will need to use their judgment or seek guidance from the organic lab manager or another experienced analyst to decide if the analyte is there.

7.9.2 Multi-peak components (PCB's, Toxaphene and Technical Chlordane) are identified by pattern recognition using an on scale standard chromatogram to compare to an on scale sample chromatogram enabling the analyst to judge whether the sample pattern matches a standard pattern. Confirmation of multi-peak components is required by the method and may be accomplished in several ways. If the sample is from a source known to contain specific Aroclors then this information may be used as a confirmation. Documentation of this approach must meet the requirements outlined in Sec. 7.7.3 of SW-846 Method 8082. Another approach is to use a column of dissimilar stationary phase and compare the pattern to a known Aroclor standard. Finally if the concentration is high enough GC/MS may be used as confirmation.

7.9.2.1 Generally, five unique peaks representing the full range of the multi-peak component are used in the quantitation of the multi-peak components. Note: for USACE projects, five peaks are necessary for the quantitation of multi-peak components.

7.9.2.2 Multi-peak components that still have matrix interference after appropriate sample cleanup steps have been taken may need to be hand calculated using peaks that do not have interference. This should be brought to the organic lab manager's attention.

7.9.2.3 Multi-peak components that exhibit a weathered pattern may need to be hand calculated by the analyst. The analyst will need to use peaks that exhibit the full range of weathering. The number of peaks used to quantitate the multi-peak component will depend on the analyst's judgment of what it will take to achieve the truest concentration of the component. This should be brought to the organic lab manager's attention.

7.9.3 Quantitation – Once a compound has been identified qualitatively, the concentration must then be quantitated. If the RSD of the compound's response factor is 20% or less, then the concentration may be determined using the mean calibration factor, CF, from the initial calibration data. Otherwise, the analyst must use either a calibration curve or a non-linear calibration model such as polynomial equation for quantitation. Calculations follow in Section 8.0.

8.0 Calculations:

8.1 Calculate the calibration factor (CF) for each analyte at each concentration as:

$$CF = \frac{\textit{Peak Area (or Height) of the Compound in the Standard}}{\textit{Mass of the Compound Injected (in nanograms)}}$$

8.2 The mean CF is calculated as follows:

$$\overline{CF} = \frac{\sum_{i-1}^{n} CFi}{n}$$

8.3 The standard deviation (SD) and the relative standard deviation (RSD) of the calibration factors for each analyte are calculated as follows:

$$SD = \sqrt{\frac{\sum_{i-1}^{n} (CFi - \overline{CF})^2}{n-1}}$$

$$RSD = \frac{SD}{CF} \times 100$$

8.4 Calibration verification involves the calculation of the percent drift (linear or quadratic) or the percent difference (average) of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference, depending on the calibration procedure used.

$$\%\ \text{Drift} = \frac{(\text{Calculated concentration} - \text{Theoretical concentration}) * 100}{\text{Theoretical Concentration}}$$

where the calculated concentration is determined from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{(\text{CCV CF} - \text{Average CF}) * 100}{\text{Average CF}}$$

where CCV CF is the calibration factor from the analysis of the verification standard and mean CF is the average calibration factor from the initial calibration. The % difference or % drift calculated for the calibration verification standard must be within ±15% for each analyte before any sample analyses may take place.

8.5 Concentration in water samples is calculated as follows:
[Note: Using the units specified here for these terms will result in a concentration in units of ng/mL, which is equivalent to µg/L.]

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(V_s)}$$

where:

A_x = Area (or height) of the peak for the analyte in the sample.
V_t = Total volume of the concentrated extract (µL).
D = Dilution factor, if the sample was diluted prior to analysis. If no dilution was made, D = 1. The dilution factor is always dimensionless.
V_i = Volume of the extract injected (µL). The nominal injection volume for samples and calibration standards must be the same.
CF = Mean response factor from the initial calibration.
V_s = Volume of the aqueous sample extracted (mL). If units of liters are used for this term, multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL. If the injection (V_i) is expressed in mL, then the 1000 may be omitted.

8.6 Concentration in non-aqueous samples is calculated as follows:
[Note: Using the units specified here for these terms will result in a concentration in units of ng/g, which is equivalent to µg/kg.]

$$\text{Concentration } (\mu\text{g/kg}) = \frac{(A_x)(V_t)(D)}{(\overline{CF})(V_i)(W_s)}$$

where:
A_x, V_t, D, and CF are the same as for aqueous samples, and
W_s = Weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term multiply the results by 1000.

The 1000 in the denominator represents the number of µL in 1 mL. If the injection (V_i) is expressed in mL, then the 1000 may be omitted.

9.0 QUALITY ASSURANCE/QUALITY CONTROL/CORRECTIVE ACTIONS

9.1 Surrogates - All samples and QC are spiked with surrogates. The surrogate recoveries from method blanks and LCS are charted to generate control limits and charts for diagnostic purposes. 8000B See section 7.8.5 above for criteria and corrective action.

9.2 LCS Sample - The LCS is extracted with every extraction batch - up to 20 samples. To prepare the LCS, a blank is spiked with standards prepared from an alternate vendor or lot number than the calibration standards. The recoveries are charted to generate control charts and limits. See the LCS report form in the appendix for the laboratory generated limits. These limits default to method limits if generated limits are wider. If the LCS compound has a recovery above the upper limit, but the same compound is not detected in any of the batch samples, no corrective action is required. For all other situations, the LCS should be reanalyzed for the failed analytes only or results for that analyte should be flagged. If the second analysis fails, all associated samples should be reextracted/reanalyzed for the failed analytes only. **DOD limits will be used for DOD QSM Ver.3 projects.**

9.3 Method Blanks - The concentration of all method target analytes should be below the MDL **(<RL, common laboratory contaminates; < ½ RL, all other compounds or client/authority specified)** for each method target analyte. If contamination exceeds the requirement, the following corrective actions must be taken. The first step is to assess the effect on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps should be taken to find/reduce/eliminate the source of this contamination in the method blank. If an analyte is found in the method blank and some, or all, of the other batch samples, then corrective action is required. The source of contamination must be investigated and appropriate action taken and documented to find/reduce/eliminate the source of this contamination. The method blank, and any samples containing the same contaminant, would likely be reextracted/reanalyzed. For the common laboratory contaminants, meeting the above requirements is not practical. Random cases of contamination are difficult to control, however, daily contamination is not acceptable and corrective action is essential. If a contaminant is found in the method blank and the samples, the compound concentration must be flagged with a 'B' on the final report unless the concentration is greater than 5x that found in the method blank.

9.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample - 1 in 20 samples are spiked for a MS/MSD (for 608 projects, 1 in 10 samples are spiked for MS). For project specified full list MS/MSDs, the LCS standard is used for spiking. Criteria for the MS/MSD are found in Table 5-3 of the Laboratory Quality Assurance Manual. Both the percent recoveries (%R) and relative

percent differences (RPDs) are contained in this table (for project specified full list MS/MSDs, the MS/MSD limits are the same as the LCS limits). Samples that do not meet these criteria due to matrix should be evaluated for placing a flag on the final report due to QC problems. The associated LCS results should be used to verify method performance (section 8.4.3 Method 8081A). MS data evaluation must include the consideration of the following factors.

9.4.1 Sample matrix - If the sample is a soil, grab sample or sequentially collected water sample it may affect the %R and RPD of the MS/MSD. Corrective action must be taken in the form of reanalysis if a method problem is indicated.

9.4.2 Original sample concentration - If a spiked compound has a problem and the concentration of that compound in the original sample was more than four times the concentration of the spike, no further corrective action may be necessary other than the generation of a corrective action report to document the problem. In this case, the MS/MSD may be evaluated as sample duplicates.

9.4.3 MS vs. MSD - If a spiked compound has a similar problem in both the MS and MSD and is not traced to a method problem, no further action may be necessary other than the generation of a corrective action report to document the problem.

9.4.4 Non-target Interference - The presence of significant non-target interference should be brought to the immediate attention of your supervisor who should discuss the problem with the client/project manager to determine the action to be taken.

9.4.5 Documentation of capability (DOC) – Each analyst must perform a DOC to demonstrate proficiency with this method. Refer to SOP-413 for guidance.

10.0 HEALTH, SAFETY, WASTE MANAGEMENT AND POLLUTION PREVENTION

10.1 Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of blue nitrile gloves and lab coats is highly recommended.

10.2 Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples that need special consideration have applicable notes on the sample logs.

10.3 MSDS sheets are available for all reagents and standards that have been purchased. These are located in the bookshelves across from the Quality Assurance Officers cube.

10.4 Please see Waste Disposal, SOP-210 and SOP-405 for proper disposal of waste coming from this area within our laboratory. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

11.0 EXAMPLE FORMS

Examples of the water and soil LCS report sheet and the USACE analyst data review checklist are located in the appendix.

12.0 REFERENCES

1. *Test Methods for Evaluating Solid Waste Physical/Chemical Methods, SW-846; Third Edition (Update III)*; Method 8081A, 8082

2. USEPA *Code of Federal Requlations, 40, CH 1,PT 136;* Method 608, 608.2; APX-B

3. USEPA *Contract Laboratory Program(CLP) for Organics ILM04.2; ILM04.3*

APPENDIX

FORM 3
WATER PESTICIDE/PCB LAB CONTROL SAMPLE
(In- House)

Lab Name: Empirical Laboratories, LLC Contract:

Lab Code: NA Batch No.: NA SAS No.: NA SDG No.:

Matrix Spike - Client Sample No.: LCS

COMPOUND	SPIKE ADDED (µg/L)	SAMPLE CONCENTRATION (µg/L)	LCS CONCENTRATION (µg/L)	LCS % REC #	QC. LIMITS REC.
Aldrin	0.05000	NA	0.05000	100	25-110
alpha-BHC	0.1000	NA	0.1000	100	45-125
alpha-Chlordane	0.05000	NA	0.05000	100	50-125
beta-BHC	0.05000	NA	0.05000	100	50-130
4,4'-DDD	0.1000	NA	0.1000	100	55-130
4,4'-DDE	0.1000	NA	0.1000	100	45-130
4,4'-DDT	0.1000	NA	0.1000	100	50-140
Dieldrin	0.1000	NA	0.1000	100	55-130
delta-BHC	0.05000	NA	0.05000	100	40-135
Endosulfan I	0.1000	NA	0.1000	100	50-120
Endosulfan II	0.1000	NA	0.1000	100	55-135
Endosulfan sulfate	0.1000	NA	0.1000	100	55-130
Endrin	0.1000	NA	0.1000	100	40-150
Endrin aldehyde	0.1000	NA	0.1000	100	40-130
Endrin ketone	0.1000	NA	0.1000	100	60-130
gamma-BHC (Lindane)	0.1000	NA	0.1000	100	50-130
gamma-Chlordane	0.05000	NA	0.05000	100	50-125
Heptachlor	0.1000	NA	0.1000	100	35-125
Heptachlor epoxide	0.05000	NA	0.05000	100	50-130
Methoxychlor	0.5000	NA	0.5000	100	50-140
PCB-1248	10.00	NA	10.00	100	50-140

Column to be used to flag recovery values with an asterisk

* Values outside of QC limits

Spike Recovery: 0 out of 21 outside limits

COMMENTS: _____

FORM 3
SOIL PESTICIDE/PCB LAB CONTROL SAMPLE
(In-House)

Lab Name: Empirical Laboratories, LLC Contract:

Lab Code: NA Batch No.: NA SAS No.: NA SDG No.:

Matrix Spike - Client Sample No.: LCS

COMPOUND	SPIKE ADDED (µg/kg)	SAMPLE CONCENTRATION (µg/kg)	LCS CONCENTRATION (µg/kg)	LCS % REC #	QC. LIMITS REC.
Aldrin	5.0000	NA	5.0000	100	30-135
4,4'-DDT	10.000	NA	10.000	100	30-160
Dieldrin	10.000	NA	10.000	100	30-150
Endrin	10.000	NA	10.000	100	35-160
gamma-BHC (Lindane)	10.000	NA	10.000	100	30-145
Heptachlor	10.000	NA	10.000	100	40-150
PCB-1248	1000.0	NA	1000.0	100	50-150

Column to be used to flag recovery values with an asterisk

* Values outside of QC limits

Spike Recovery: 0 out of 7 outside limits

COMMENTS: _____

page 1 of 1 FORM III PEST

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):	
Batch Number(s):	
Method:	**8081A/8082**

QA/QC Item	Yes	No	NA	Second Level Review
A. Initial Calibration				
1. Did the evaluation mix pass criteria?				
2. Does the curve consist of at least five Calibration Standards?				
3. Is the low standard near, but above the MDL?				
4. Are the % RSDs within QC limits for all analytes?				
B. Second Source Verification				
1. Was the initial calibration curve verified by a second source calibration standard (ICV) and have criteria been met?				
C. Continuing Calibration				
1. Are the Continuing Calibration Verification (CCV) standards analyzed every 20 samples or every 12 hours and at the end of the sequence?				
2. Are the % differences within QC limits for all analytes?				
D. Sample Analysis				
1. Did the evaluation mix pass criteria?				
2. Are all sample holding times met?				
3. Are all samples with concentrations > the highest standard used for initial calibration diluted and reanalyzed?				
4. For single peak analytes - are all compounds identified on the primary column confirmed on the secondary column?				
5. For multi-peak analytes - does the pattern of the analyte in the sample match the pattern of the standard?				

6. Are surrogate recoveries within QC limits? (one surrogate both columns) _____ _____ _____ _____

ANALYST DATA REVIEW CHECKLIST

E. QC Samples

1. Is the Method Blank extracted at the desired frequency and is its concentration for target analytes less than the MDLs? _____ _____ _____ _____
2. Is the Laboratory Control Sample and its percent recovery within QC limits? _____ _____ _____ _____
3. Is the Matrix Spike/Matrix Spike Duplicate extracted at the desired frequency and is the percent recovery/RPD within QC limits? _____ _____ _____ _____

F. Others

1. Are all nonconformances included and noted? _____ _____ _____ _____
2. Are all calculations checked at the minimum frequency? _____ _____ _____ _____
3. Did analyst initial/date the appropriate printouts and report sheets? _____ _____ _____
4. Are all sample IDs and units checked for transcription errors? _____ _____ _____ _____
5. Are all manual integrations checked by a second reviewer to verify they were performed correctly? _____ _____ _____ _____

Comments on any "No" response:

_____

_____

_____

_____

_____

_____

Analyst: _____ Date: _____

Second-Level Review: _____ Date: _____

GC DATA AND REPORT CHECK

SOP NUMBER: SOP-216

REVISION NUMBER: 8

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: 8/03/05

DATE OF LAST REVIEW: 8/03/05

GC DATA AND REPORT CHECK

I. SUMMARY

The following describes the process through which the data and report is checked after being quantitated by the HP Chemserver 4920 data system.

A. Data Format

The Target DB Windows NT data system generates a report, which contains the following:

1. Quantitation Report - This includes sample identification, date and time analyzed, instrument identification, file information and compound information (compound name, retention time, area counts, calculated concentration based on the calibration curve and final concentration based on sample factors).

2. Chromatogram - A graphic representation of the GC analysis including peak integration. A blowup of the chromatogram is appropriate if it is being scaled too small to see the main peaks.

B. Primary Analyst Check

The primary analyst is responsible for checking that the sample meets all the appropriate method criteria, confirming the identification of all analytes and generating a summary report. If criteria are not met, a Non-Conformance Report (NCR) is entered on the form within 24 hours and the organic manager is notified.

1. Surrogates: Percent recoveries must meet in-house limits for the analysis type and matrix. In-house limits are generated annually from a minimum of 20 LCS and method blank data points. A non-conformance report must be entered on the form if the recoveries are outside the in-house limits. The sample must be flagged if the recoveries are outside in-house limits (unless the sample is NPDES which has no designated surrogate recovery criteria). For pest/PCB samples, only one of the two surrogates added must meet the limits for the sample to be considered in control as long as the second surrogate has >10% recovery.

2. Target analyte identification is checked on dual column analyses to see that it is confirmed and on single column analyses to see that the pattern matches. The experience of the operator is invaluable in this identification process.

3. Target analyte quantitation is checked to make sure the proper units have been calculated and all the factors used are correct.

4. Supporting documentation will be supplied in the case of any analyte identification, which is questionable, or for any other reason the operator deems necessary. The experience of the operator is invaluable in this process.

5. After checking the data, each quantitation report is initialed and dated.

6. At this point, a summary report is generated.

7. Following summary report generation, it is checked against the quantitation report for calculations and units. It is checked for client and sample information (Client ID, Sample ID, Client list/report, Special requests, etc.). The report is also compared to historical data, if available. It is then initialed and dated.

8. The report is sent forward for second check with all data, necessary QC and NCR's. The data checklist is completed and sent forward as well.

C. Secondary Analyst Check

The secondary analyst is responsible for checking the primary analyst on target identification and quantitation. If a discrepancy is noted, the secondary analyst will notify the primary analyst about all corrections. The primary analyst will make all corrections, then the corrections will be verified once again by the secondary analyst. The secondary analyst completes the data checklist.

1. All target analyte identifications and calculations must be verified using the criteria given above and the quantitation report initialed and dated.

2. The report is checked to make sure all client and sample information is correct then sent forward with all necessary data, QC, data checklist and NCR's to generate a report.

D. Report Generation

The Organic Report Specialist confirms data are organized and a report is generated with the appropriate client list and all required client QC. All calculations from the quant report to the summary report are checked. Also, all report information is checked, including the client information, units, sampling and receiving dates, sample identification and the presence of all necessary target analytes. The summary report is initialed and dated at this time then forwarded to the appropriate Project Manager (PM). The PM checks the report for completeness and forwards it to the administrative assistant.

E. Administrative Assistant Check

The Administrative Assistant is responsible for printing the final report on letterhead. After this step, the administrative assistant returns it is to the PM.

F. Project Manager Check

The PM checks the report to make sure it is in the format required for the client. The analyte list and the QC are also checked. The report is evaluated for conflicting or unusual results. Items, which seem questionable are checked against the data and/or discussed with the analyst. The report is then forwarded to the division director to be evaluated and signed. The report is returned to the PM who mails out the final report and generates the invoice.

TOTAL ORGANIC CARBON (TOC)

SM5310C, USEPA METHOD 415.1 SW846 METHOD 9060 AND Lloyd KAHN METHOD

SOP NUMBER: SOP-221

REVISION NUMBER: 5

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 11/29/06

DATE OF LAST REVIEW: 11/29/06

TOTAL ORGANIC CARBON (TOC)
BY SM5310C, EPA METHOD 415.1, SW846 METHOD 9060 AND Lloyd KAHN
METHOD "*DETERMINATION OF TOC IN SEDIMENT*"

I. SCOPE AND APPLICATION

This SOP describes the measurement of TOC by SM5310C, EPA Method 415.1, SW-846 Method 9060 and Lloyd Kahn Method for determination in soil / sediment matrix.

SM5310C is used to determine the concentration of organic carbon in source and drinking water, EPA Method 415.1, SW-846 Method 9060 are used to determine concentrations of carbon in saline waters, domestic and industrial wastes and SW846 Method 9060 is modified for soil determination and the Lloyd Kahn Method is used for determination of TOC in soil/sediment and solid matrices. SW846 Method 9060 and the Lloyd Kahn Method require quadruplicate analysis of samples, where as SM5310C and 415.1 only require single analysis. These methods should be read over carefully by the analyst and any restrictions should be noted.

II. SUMMARY OF METHOD

The organic carbon is measured using an OI Analytical Carbon Analyzer model 700 (aqueous samples) and an OI Analytical Solids TOC Analyzer model 1010 (soil/sediment samples). The model 700 instrument converts the organic carbon in a sample using wet chemical oxidation. The CO_2 formed is then measured by an infrared detector (replaces ultraviolet detector in SM 5310C). With the model 1010 Solids TOC analyzer, TOC is determined by acidifying a sample and heating it to 250°C to remove the TIC. The sample is then heated to 900°C to combust the remaining TOC. The resulting carbon dioxide from the TOC is detected by a non-disperse infrared (NDIR) detector that has been calibrated to directly display the mass of carbon dioxide detected. This mass is proportional to the mass of TOC in the sample.

The limit of detection for the water method is 0.60 mg carbon/L and the Limit of quantitation is 1.0 mg carbon/L. The limits of detection and quantitation with the soil method depends on the how many grams of sample is used for the analysis. For a 250 mg sample the limit of detection is 460 mg/kg and the limit of quantitation is 1600 mg/kg.

III. SAMPLING HANDLING AND PRESERVATION

3.1 Sampling and storage in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples. NOTE 1: A brief study performed in the EPA Laboratory

indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

3.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. The holding time is 28 days for waters and soils with the exception of the Lloyd Kahn method soils, which requires a 14 day holding time. Also, samples must be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

3.3 When water samples cannot be analyzed immediately, the sample is preserved by acidification to (pH </= 2) with HCl or H_2SO_4. Both water and soil samples are stored at 4°C.

IV. INTERFERENCES

4.1 WATER METHOD

4.1.1 Removal or carbonate and bicarbonate carbon by acidification and purging with purified gas results in the loss of volatile organic substances. The volatiles also can be lost during sample blending, particularly if the temperature is allowed to rise. Another important loss can occur if large carbon-containing particles fail to enter the needle used for injection. Filtration although necessary to eliminate particulate organic matter when only DOC is to be determined, can result in loss or gain of DOC, depending on the physical properties of the carbon-containing compounds and the adsorption of carbonaceous material on the filter, or its desorption from it. Check filters for their contribution to DOC by analyzing a filtered blank. Note that any contact with organic material may contaminate a sample. Avoid contaminated glassware, plastic containers, and rubber tubing. Analyze treatment, system, and reagent blanks.

4.1.2 This procedure is applicable only to homogenous samples which can be injected into the apparatus reproducibly by means of a pipette. The openings of the pipette limit the maximum size of particles which may be included in the sample.

4.2 SOIL METHOD

4.2.1 All materials must be routinely demonstrated to be interference –free under the analysis conditions by running blanks. Use high purity or purified reagents and gases to help minimize interference problems.

4.2.2 The infrared detector is sensitized to CO_2 and accomplishes virtually complete rejection of response from other gases that absorb energy in the infrared region.

V. DEFINITIONS

5.1 ANALYTICAL BATCH-The set of samples extracted /distilled/ or digested at the same time to a maximum of 20 samples.

5.2 CALIBRATION BLANK (CB)- A volume of reagent water in the same matrix as the calibration standards, but without the analyte.

5.3 CALIBRATION STANDARD (CAL)- A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

5.4 FIELD BLANK (FMB)- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all preanalysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

5.5 FIELD DUPLICATE (FD)- Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

5.6 LABORATORY BLANK (LRB)- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to determine if the analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

5.7 LABORATORY CONTROL SAMPLE (LCS)- A solution prepared in the laboratory by dissolving a known amount of one or more pure compounds in a known amount of reagent water. Its purpose is to assure that the results produced by the laboratory remain within the acceptable limits for precision and accuracy. (This should not be confused with a calibrating standard, it must be prepared from a source other than the same source as the calibration standards).

5.8 LABORATORY DUPLICATE (LD)- Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

5.9 QUALITY CONTROL CHECK SAMPLE (QCS)- A sample containing analytes of interest at known concentrations (true value) of analytes. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory

performance using test materials that have been prepared independently from the normal preparation process.

5.10 METHOD DETECTION LIMIT (MDL)- The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

VI. REAGENTS/STANDARDS

Store all reagents and standards according to recommendations. All standards should be stored away from light and at 4°C (± 2°C).

6.1 The laboratory reagent blank water used for TOC analysis is obtained from the Modulab Analytical water purification system in the analytical laboratory. **Boiling the water is not necessary as the method states.**

6.2 Potassium hydrogen phthalate, primary stock solution, 1000 mg/L: Dissolve 0.2128g of potassium hydrogen phthalate (primary standard grade) in 100.0 mL water.

6.3. Potassium hydrogen phthalate, standard solutions : A 100 mg/L standard is prepared by transferring 10 mL of the stock solution to a 100 mL volumetric flask and diluting to the mark with water. This solution is prepared on a daily basis.

6.4. The carbonate-bicarbonate solutions are not needed for this instrument.

6.5 Calibration Standards

1. For the water method, calibration standard is Potassium Hydrogen Phthalate. Standards are made from dilutions of the stock 1000 mg/L standard as follows:

   1.0 mg/L = 0.10 mL of 1000 mg/L -> 100 mL
   2.5 mg/L = 0.25 mL of 1000 mg/L -> 100 mL
   5.0 mg/L = 0.50 mL of 1000 mg/L -> 100 mL
   10.0 mg/L = 1.0 mL of 1000 mg/L -> 100 mL
   25.0 mg/L = 5.0 mL of 1000 mg/L -> 200 mL
   50.0 mg/L = 10.0 mL of 1000 mg/L -> 200 mL

   A low level standard curve must be run for drinking water samples with the standards made as follows:

   0.25 mg/L = 0.025 mL of 1000 mg/L -> 100 mL
   0.50 mg/L = 0.050 mL of 1000 mg/L -> 100 mL

1.0 mg/L = 0.10 mL of 1000 mg/L -> 100 mL
1.5 mg/L = 0.15 mL of 1000 mg/L -> 100 mL
2.5 mg/L = 0.25 mL of 1000 mg/L -> 100 mL
5.0 mg/L = 0.50 mL of 1000 mg/L -> 100 mL
10.0 mg/L = 1.0 mL of 1000 mg/L -> 100 mL

2. The soil method the calibration standard is prepared by using an OI commercially prepared 30% carbon sucrose solution.

6.6 Laboratory Control Sample:

1. For the water method, the Laboratory Control Sample is normally made from a performance evaluation solution in which the true value is known. This solution is given a unique identifier.

2. For the soil method, the Laboratory Control Sample is made from a 30% sucrose solution which is made by weighing up 7.125 grams of EM Reagent Grade Sucrose and diluting to 10 mL with deionized water volumetrically.

6.7. Sodium persulfate oxidation solution: This solution is made by dissolving 100g of sodium persulfate in 1000 mL of water.

6.8 Phosphoric acid solution 5%: Dilute 59 mL of concentrated 85% phosphoric acid in 1000 mL of water. This is used for both water and soil methods.

VII. INSTRUMENTATION

7.1 The instrument used for the Water TOC analysis is an OI 700 series Carbon Analyzer. An OI 1010 soil/sediment carbon analyzer is used for soil samples.

7.2 There is an OI corporation autosampler attached to the OI 700 which will hold 96 samples.

7.3 The corresponding millivolt reading for each sample is printed on a Citizen's Dot Matrix, model AH10-M0124 printer for the water samples. The soil/sediment data are printed out at the organic GC printer.

VIII. AQUEOUS SAMPLE PROCEDURE

This is a step by step description of a routine aqueous TOC analysis.

8.1 Wearing labcoat, gloves and safety glasses, the standards and check solutions should be taken out of the refrigerator and allowed to warm to room temperature. Also, remove samples from sample storage signing them out

appropriately on the internal chain of custody form. Fresh acid and oxidation solutions should be poured into the appropriate containers on the front of the instrument. The nitrogen should be turned on and the regulator set at 30 psi.

8.2 The instrument should now be turned on. This is accomplished by pulling the control panel on the front of the instrument down and pressing the number one on the panel as the power switch is turned on. At this point the instrument should be allowed to warm up for 5 to 10 minutes. The display will change from standby to ready. Consult pages 57-78 in the OI 700 instrument manual for illustrations of the instrument and explanations of the keys on the control panel.. The printer is always left on and the first and third green lights on the front should be lit.

8.3 Prepare 20 laboratory reagent water blanks in the disposable cuvettes that fit into the autosampler. Approximately 10 mL of water should be placed in each tube. The tubes should be placed in the autosampler and advanced to the first position by pressing the button on the lower right hand side of the autosampler.

8.4 The acid and oxidation solutions are now primed by pushing either the prime acid or prime oxid keys on the front panel about 20 times each. The tubing going into each solution should be monitored for air bubbles. The priming keys should be pushed until no more air can be seen in the tubing.

8.5 Press the **SET SYSTEM CONFIG** button and the display will change to read Select Section 1,2,or3. Select section "2" and then ENTER. Set the first sample to "01" ENTER, the last sample to "20" (or the last number in the sample sequence) ENTER, and the number of replicates to "1" ENTER. Hit ENTER now until you see the original ready display. Now hit the red **RUN/STOP** key. The instrument will now run the blank water solutions.

8.6 The last two or three blanks should have millivolt readings between - 7.0 and + 7.0. If the values are not in this range then follow this procedure. Hit the **SELECT ANALYSIS MODE** twice to bring the instrument display to Calibrate Constants, Calibration. Hit the "2" button and then hit ENTER twice to bring it to OC blank on the readout. If the millivolt readings obtained on the blanks were too low then lower the OC blank by one or two. If the millivolt readings obtained on the blanks were too high then raise the OC blank by one or two(see OI 700 instrument manual pages 57-78). Then run 5 more blanks to make sure the millivolt readings meet the above criteria.

8.7 **Following is a list outlining the order in which the samples should be run.** Each sample tube should be numbered and its identity entered into the TOC log book. Note: All blanks should be acidified to pH 2 to match the matrix of the samples analyzed.

1. Water Blank
2. Water Blank
3. 1.0 ppm
4. 1.0 ppm
5. Water Blank
6. Water Blank
7. 2.5 ppm
8. 2.5 ppm
9. Water Blank
10. Water Blank
11. 5.0 ppm
12. 5.0 ppm
13. Water Blank
14. Water Blank
15. 10 ppm
16. 10 ppm
17. Water Blank
18. Water Blank
19 25 ppm
20. 25 ppm
21. Water Blank
22. Water Blank
23. 50 ppm
24. 50 ppm
25. Water Blank
26. Water Blank
27. Method blank
28. Water Blank
29. Water Blank
30. LCS + 9 samples (including any sample QC) with 2 water blanks between the LCS and each sample
31. 25 ppm
32. Water Blank
33. Water Blank
34. 10 samples (including any sample QC) with 2 water blanks between each sample
35. 25ppm

8.8 The Excel file for calculations is located in "V:\WCM\TESTS\TOC". The sample identity, its corresponding millivolt reading, and the appropriate dilution factor are entered into the appropriate columns. The Excel worksheet is self explanatory. Normal procedure is followed for preparing reports and the data is second checked before being given to the supervisor.

IX. SOIL/SEDIMENT SAMPLE PROCEDURE

A sample is introduced into the Solid Module via a conditioned sample cup. Once the sample has been introduced the entire analysis sequence is automatic. Please reference Chapter 4 of the OI 1010 Solid Module instrument manual for instrument states and configuration when initially setting the instrument methods up.

TC Mode Instrument Settings:

Analysis Temp:900°C
Analysis Time: 6.5 minutes
Nitrogen Gas Flow: 60-100 psi (external regulator regulator)
Oxygen Gas Flow: 40-60 psi (external regulator)

This is a step by step description of a routine soil TOC analysis.

9.1 The standards and check solutions should be taken out of the refrigerator and allowed to warm to room temperature. The nitrogen and oxygen (internal regulator should be set at 50-60 psi) turned on allowing a nitrogen flow of 350-400mL/minute and an oxygen flow of 180 mL/minute (± 3 mL/minute).

NOTE: DO NOT TURN THE ANALYZER ON BEFORE TURNING THE GAS ON!

9.2 Let the gas flow through the instrument for a few minutes. The instrument should now be turned on and let to stabilize for 30 minutes.

9.3 Condition the cups (with quartz wool in them) using Diagnostics under Instrument Menu commands, (don't condition too many cups at a time since setting in contact with the air can cause contamination).

9.4 Set up the subdirectory (using the current date to ID it) under WinTOC output.

9.5 If doing an initial calibration curve use an appropriate µL syringe to make the following measurements of the sucrose standard in order to achieve the indicated concentrations. Make sure that there are no air bubbles in the syringe. Turn the syringe with the needle pointed up and vibrate the barrel and disperse any air from the syringe. To enter the calibration information on the instrument go to Instrument Cal Menu, type in the calibration standard values and save the file as the cal.. date analyzed.

µL 30% Sucrose STD	Concentration (mg)
0	0
2.0 (1:6 solution)	0.10

3.0	0.90
50	15
100	30

Note: The 1:6 solution of the 30% Sucrose standard is prepared by mixing 100µL of the 30% Sucrose standard with 500µL of water.

9.6 Enter the sequence to be analyzed as listed below:

1. CCV(CCV1+ date analyzed for ID) or Initial calibration – single analyses
2. Method Blank(MB + date analyzed for ID) – single analyses
3. LCS, 15 mg dextrose (LCS + date analyzed for ID) – single analyses
4. NY Cert – 4 replicates
5. Sample – 4 replicates
6. Sample – 4 replicates
7. Sample – 4 replicates
8. Sample – 4 replicates
9. Sample – 4 replicates
10. CCV(CCV1+ date analyzed for ID)2 – single analyses
11. Sample – 4 replicates
12. Sample – 4 replicates
13. Sample – 4 replicates
14. Sample – 4 replicates
15. Sample – 4 replicates
16. CCV (CCV2+ date analyzed for ID) – single analyses
17. Sample – 4 replicates
18. Sample – 4 replicates
19. Sample – 4 replicates
20. Sample – 4 replicates
21. Sample – 4 replicates
22. CCV(CCV3+ date analyzed for ID) – single analyses
23. Sample – 4 replicates
24. Sample – 4 replicates
25. Sample – 4 replicates
26. Sample – 4 replicates
27. Sample – 4 replicates
28. CCV(CCV4+ date analyzed for ID) – single analyses
29. SampleMS – 4 replicates
30. SampleDUP – 4 replicates
31. FCV(CCV4+ date analyzed for ID) – single analyses
32. FCB(FCB4+ date analyzed for ID) – single analyses

9.7 Samples should be stored away from light and at 4°C (± 2°C). Wearing labcoat, gloves and safety glasses remove samples from sample storage signing them out appropriately on the internal chain of custody form.

9.8 Transfer a homogeneous aliquot(~5 g) of the sample into a small pre-labeled aluminum weighing pan. Label each pan with the appropriate sample ID then add enough phosphoric acid (1-2 ml) to remove the Total inorganic carbon (TIC) when the sample is placed in an oven at 250°C. Place the samples in the 250°C oven for 10 minute and begin prepping the sample cups to weigh 0.2g-1.0g of each sample(in quadruplicate). Limit the time that the cups are exposed to the atmosphere as to reduce potential contamination. **Note: Since the samples are dried in this manner, before the sample aliquot it taken, a % solids determination and calculation is NOT necessary to report the sample concentrations in dry weight.**

9.9 Set the OI 1010 to the TC Mode and start running the sequence beginning with the initial calibration or calibration verification standard as illustrated above. Weigh each sample in quadruplicate making sure to limit the time that samples are exposed to the atmosphere.

9.10 The Excel file for calculations is located in "V:\WCM\TESTS\TOC soil\". The sample identity, its corresponding mgC reading, and the sample weight are entered into the appropriate columns. The Excel worksheet is self explanatory. Normal procedure is followed for preparing reports and the data is second checked before being given to the supervisor.

X. QC REQUIREMENTS

10.1 Analyze a laboratory control sample (LCS) for each batch of samples (maximum of 20 samples per day). If the LCS does not fall within the control limits of 80 to 120%, corrective action must be taken to find and correct the problem.

10.2 Run a method blank (PB) for each batch of samples (maximum of 20 samples per day). The PB should be less than 1/2 the reporting limit.

10.3 One matrix spike and matrix spike duplicate must be run per set of 20 samples. For water analysis, a spike and spike duplicate are made by mixing 9.85 mL of sample with 0.15 mL of 1000 mg/L standard using an ependorf pipette. The percent recoveries on a MS and a MSD should be within 75 and 125%. Relative percent difference (RPD) on duplicates should be less than 20%. If not, a corrective action (CAR) must be approved by your supervisor.

10.4 Analyze an initial calibration verification (ICV) immediately after the calibration curve. Analyze a calibration check verification (CCV) standard every tenth sample and at the end or after every fifth sample when analyzing samples in quadruplicate. Analyze a CCV after every 5th sample when analyzing soil/sediment samples. The percent recoveries should be in the

range of 90 to 110%. The CCV %RSD warning limits are ≤15% for aqueous samples and ≤20% for soil/sediment samples. If the CCV % RSD exceeds 15%(aqueous) or ≤30% (soil/sediment) and the correlation coefficient is less than 0.990 correct the problem and re-analyze the CCV.

10.5 When analyzing water samples, all water blanks before samples and standards must be below the detection limit, otherwise the samples must be rerun.

10.6 Analyze an initial calibration blank (ICB) following the ICV. Analyze a continuing calibration blank (CCB) following each CCV. The ICB and CCB should be less than ± the MDL.

10.7 Calculate all percent recoveries and relative percent differences on duplicates and show calculations on data.

10.8 Calculate all percent recoveries and relative percent differences on duplicates and show calculations on data.

Calculate spikes as follows where everything is in concentration.

$$\% \text{ Recovery} = \frac{\text{Spike} - \text{Sample}}{\text{True Value}} \times 100$$

Relative percent difference is calculated as follows, with everything in concentration:

$$\text{RPD} = \frac{\text{Higher Concentration} - \text{Lower Concentration}}{\text{Average of Concentrations}} \times 100$$

10.9 SM5310B and EPA Method 415.1 require a single analyses per sample but SW-846 Method 9060 requires quadruplicate analysis of each sample. The Loyd Kahn soil method suggests 1 sample per 20 be run in quadruplicate. Some clients may request that all samples to be done in quadruplicate. Please check with your supervisor if you have any questions about the required numbered of sample replications.

10.10 **For aqueous samples check an acidified 20mg/L inorganic carbon standard quarterly, to assure that purge gas flow is adequate to remove inorganic carbon. The result should be below the reported quantitation limit.**

XI. CORRECTIVE ACTIONS

11.1 INSTRUMENT RELATED

1. ICV not within ± 20% (Soil) or ± 10% (415.1)
   a. If the problem is with the solution.
      i. Re-prepare, obtain new stock if necessary.
   b. If the problem is with the calibration.
      i. Recalibrate through analysis of appropriate standards and recheck ICV.
2. CCV not within ± 30% (Soil) or ± 15% (415.1)
   a. If the problem is with the solution.
      i. Re-prepare, obtain new stock if necessary.
   b. If the problem is with the calibration.
      i. Recalibrate through analysis of appropriate standards and re-prepare / reanalyze the previous ten sample according the following guidelines.
         a. If the CCV was biased high, any of the previous ten samples which were below the minimum detection limit do not require reanalysis.
         b. If the CCV was biased low, the previous ten samples must be reanalyzed.

* **Incorrectly set gas flow is a common instrument related problem which requires corrective action. Verify that all gas flows are adjusted properly.**

11.2 SAMPLE MATRIX RELATED

1. Replicate analysis RPD not within ±20% aqueous or ±50% soil/ sediment
   i. The associated sample data must be qualified on the final report.
2. Spike analysis recovery not within ±25% aqueous or ±50% soil/ sediment
   i. If the analyte level in the sample is greater than 4X the spiking level, the %recovery can not be evaluated and no action is taken.
   ii. If the analyte level in the sample is not greater than 4X the spiking level, the associated sample data must be qualified on the final report. A corrective action report must accompany the data and be emailed or given to the supervisor.

XII. HEALTH AND SAFETY

A. Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of blue nitrile gloves and lab coats is highly recommended.

B. Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples which need special consideration have applicable notes on the sample logs.

C. MSDS are available for all reagents and standards, which have been purchased. These are located in the administrative section next to the break room.

D. Please see *Waste Disposal; SOP-405* for proper disposal of the waste generated from this area.

XIII. WASTE DISPOSAL and POLLUTION PREVENTION

Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

XIV. METHOD PERFORMANCE

14.1 Precision and Bias for Total Organic Carbon (TOC) by Persulfate-Ultraviolet Oxidation. (Water samples)

Characteristic Of Analysis Concentration determined, mg/L:	Spring Water	Spring Water +0.15 mg/L KHP*	Tap Water	Tap Water +10 mg/L KHP*	Municipal Wastewater Effluent
Replicate 1	0.402	0.559	2.47	11.70	5.88
Replicate 2	0.336	0.491	2.49	11.53	5.31
Replicate 3	0.340	0.505	2.47	11.70	5.21
Replicate 4	0.341	0.523	2.47	11.64	5.17
Replicate 5	0.355	0.542	2.46	11.55	5.10
Replicate 6	0.366	0.546	2.46	11.68	5.33
Replicate 7	0.361	0.548	2.42	11.55	5.35
Mean, mg/L	0.35	0.53	2.46	11.53	5.32
Std. Deviation: mg/L	0.02	0.03	0.02	0.21	0.23
%	6	6	1	2	4
Actual Value, mg/L	-	0.50	-	12.46	-
Recovery, %	-	106	-	93	-
Error, %	-	6	-	7	-

***KHP = potassium acid phthalate.**

14.2 There was no method performance data available for the soil procedure.

XV. REFERENCES

Annual Book of ASTM Standards, Part 31, "Water," Standard D 2574-79, p. 469 (1976).

Methods for Chemical Analysis of Water and Wastes, EPA Series Method 415.1.

Standard Methods for the Examination of Water and Wastewater, 14th ed. , p. 532, Method 505 (1975).

EPA SW-846, Method 9060.

Lloyd Kahn Method, *"Determination of Total Organic Carbon in Sediment"*

GC/MS VOLATILE NON-AQUEOUS MATRIX EXTRACTION USING SW-846 METHOD 5035 FOR 8260B ANALYSIS

SOP NUMBER: SOP-225

REVISION NUMBER: 6

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE MANAGER

EFFECTIVE DATE: 11/20/03

DATE OF LAST REVIEW: 03/16/05

GC/MS - VOLATILE
NON - AQUEOUS MATRIX EXTRACTION
USING SW-846 METHOD 5035

1.0 PURPOSE

The purpose of this SOP is to detail soil sample preparation for EPA method SW-846 5035. Soil samples should be sampled in the field using the EnCore™ sampler then shipped to the lab within 24 hours for preservation, storage and analysis. This SOP should be used in conjunction SOP-202, which details the analytical technique.

2.0 SETUP - MATERIALS NEEDED

- Sample Containers – 40mL VOA vials with low bleed septa. Available from ESS (Part No. PC0040-0300 pack of 72), alternate sources are possible but must be checked for contaminants before use. ESS also supplies pre-prepped vials with the preservative and stirbar (Part No. PC4039-5035 pack of 72).
- Varian Archon 51 position programmable autosampler, or equiv.
- Top-loading balance – capable of accurately weighing to 0.01g.
- 1-10 mL Adjustable Dispenser, Model 400 Series, Oxford pipettor. Available from Oxford (Part No. 8885-040009).
- Spatula, stainless steel – narrow enough to fit into a sample vial.
- Magnetic stirring bars – PTFE- or glass-coated, of the appropriate size to fit the sample vials. Available from A. Daigger (Part No. WX22782A, case of 50).
- EnCore™ sampler – (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent. Necessary for field sampling crew.
- Balance weights – used to calibrate the balance.
- Labels.

3.0 REAGENTS

- Reagent Water - Reagent water is NANO PURE WATER from source in the instrument lab, which is then purged with helium before use.
- Methanol, CH_3OH – purge-and-trap quality, or equivalent. Store away from other solvents.
- Sodium bisulfate, $NaHSO_4$ – ACS reagent grade, or equivalent. Available from Aldrich (Part No. 30,782-3).
- Sodium bisulfate solution – Prepare by adding 200 grams of $NaHSO_4$ (ACS reagent grade, or equivalent) to 1000 milliliters of helium-purged reagent water. Record the vendor and lot number of the $NaHSO_4$ in the Standards and Reagents Logbook. Each

standard/reagent that is prepared is recorded in the logbook and given a sequential number. The label is completed with the standard/reagent number, name, preparation date, expiration date, solvent and analyst initials. The solution should be discarded after six months or sooner if it shows signs of contamination.

4.0 SAMPLE COLLECTION

As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of volatile compounds. Always wear gloves whenever handling the tared sample vials. Several techniques may be used to perform the transfer of the sample to the relatively narrow opening of the low concentration soil vial such as the EnCore™ sampler, a cut off disposable plastic syringe, or a stainless steel spatula. We prefer to use the EnCore™ sampler.

4.1 The EnCore™ sampler is both a sampler and a container for low-level and high level soils. It is designed to collect an average weight with the exact weight to be determined in the lab. It is disposable and is also designed to have zero headspace. The EnCore™ sampler will require the field personnel to get the sample to the laboratory within 24-36 hours of collection. The laboratory needs to be contacted prior to sample collection to ensure that all necessary containers (with or without preservative) are available and that the proper sampling technique is used.

4.2 All low-level soil samples must be collected in duplicate to allow the laboratory an additional sample for reanalysis. A third sample should be collected for preparation of a high-level sample. This sample would be prepared at the same time as the "low-level" sample. (Some projects may not require the "low-level" detection limits, in this case only the high level sample preparation would be required.) A fourth sample may be collected to enable the laboratory to perform a pretest on the soil to determine if the soil sample contains carbonate minerals that will effervesce upon contact with the acidic sodium bisulfate preservative solution in the low concentration sample vial. The additional soil samples must be collected from the same soil stratum or the same section of solid waste being sampled and within close proximity to the location from which the original sample was collected. Additional bulk samples should be collected for screening and dry weight determination without the preservative. Note: If the low-level sample cannot be preserved with sodium bisulfate, the remaining low-level sample aliquot(s) is(are) transferred to a pre-weighed vial containing 5 mL of reagent water. The sample in the unpreserved vial must either be analyzed immediately (within 48 hours of collection) or frozen within the 48 hour time frame and then analyzed within the 14 day holding time.

5.0 PROCEDURE

5.1 Log-in personnel will log the samples in, place them in the Soil walk-in cooler assigned for volatile sample storage and notify the Organic Lab Manager that samples are in-house for 5035 preparation.

5.2 The Organic Lab Manager or designee will determine the amount of time remaining on the 48 hour EnCore™ holding time and assign the task of preserving the samples.

5.3 Samples received from the field should be designated for low-level, high-level or % solids/screening (this fraction should be in a regular soil jar, if it is not, it will require transfer to a VOA vial). Each low-level and high-level sample must be preserved appropriately as follows:

5.3.1 Organize the VOA vials required and label them with the sample number, date and LOW or HIGH for either low-level or high-level preservation. The LOW level VOA vials should have gray caps and septa if using the ESS brand.

5.3.2 Get the samples from the Hobart assigned for volatile sample storage and log them out.

5.3.3 Enter the sample numbers in the soil sample preparation logbook and add a sample preparation/storage blank to the book for each level being prepared (HIGH/LOW). There must be a line in the logbook for each sample vial being prepared (i.e. if there are 2 low-level samples and 1 high-level sample, the sample number should be listed in the logbook 3 times- use a,b,c to designate each vial associated with the same sample).

5.3.4 Using an adjustable Oxford pipettor, add 5-10 mL P&T methanol to each of the vials marked HIGH. Then record the vendor & lot number of methanol and the exact volume of methanol added to each sample in the sample preparation logbook. If the vial is not to be used immediately, weigh the vial to the nearest 0.01g and record the weight on the vial. The vial weight must be verified to be within ±0.01g of this value before using for sample preparation.

5.3.5 For each of the vials marked LOW, add 5 mL of sodium bisulfate solution and record the reagent number in the sample preparation logbook. Add a magnetic stir bar to each vial. If pre-prepped vials from ESS (or equivalent) are used, this step is unnecessary but the lot number and the pre-prepped status must be recorded in the preparation log.

NOTE: Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial. If the amount of gas generated is

very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and place low concentration samples in vials that contain 5ml water and a stirbar. This sample must be frozen in a slanted position until analysis or analyzed within 48 hours of sampling. Notify the Organic Lab Manager if this occurs, note this in the sample preparation logbook and generate a CAR to document the problem.

5.3.6 Place the vial (LOW/HIGH) on the top-loading balance, tare the vial then extrude the sample into the vial and record the weight of the sample in the sample preparation logbook. Make sure the lip of the vial does not have any soil on it, which might cause a leak, cap the vial tightly and mark the weight on the sample label.

5.3.7 Place the preserved samples in a box, return them to the Hobart assigned for volatile sample storage and log them back in.

6.0 ANALYSIS

Samples are analyzed by USEPA SW-846 methods 5035/8260B (low-level) using the Archon 51 position autosampler in conjunction with the GC/MS or 5030B/8260B (high-level) using any purge and trap instrument in conjunction with the GC/MS. For method 5035, the prepared low-level vials are placed in the Archon autosampler. The autosampler is programmed to add the appropriate internals and surrogates to each sample. Use of the autosampler is covered in the owners manual. Calibration of the analytical instrument with subsequent analysis of the samples is covered under SOP-202.

NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) METHOD 8330A

SOP NUMBER: SOP-327

REVISION NUMBER: 9

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE MANAGER

EFFECTIVE DATE: 07/06/06

DATE OF LAST REVIEW: 07/06/06

METHOD 8330A

NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 SCOPE AND APPLICATION

This SOP, based on SW-846 Method 8330A, is used for the trace analysis of explosives residues by high performance liquid chromatography (HPLC) using a UV-VIS detector in water, solid or sediment matrices. See SOP-431 for common environmental laboratory definitions.

2.0 SUMMARY OF METHOD

Samples are analyzed after appropriate sample preparation using HPLC with identification at 254nm on a C-18 reverse phase column and confirmation at 254nm on a Phenyl-hexyl column. The preparation is performed using a salting-out extraction procedure for low concentrations of explosives residues in water. Dilution and filtration prepare high concentration water samples for direct injection. Solid-Phase extraction, using SW-846 Method 3535, may also be applied to aqueous samples. Extraction with acetonitrile in an ultrasonic bath followed by filtration prepares soil and sediment samples.

3.0 INTERFERENCES AND POTENTIAL PROBLEMS

Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences.

2-Am-DNT and 4-Am-DNT elute at similar retention times (retention time difference of 0.2 minutes). A large concentration of one isomer may mask the response of the other isomer. If it is not apparent that both isomers are present (or are not detected), an isomeric mixture should be reported.

Degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak on the synergi column. Peak heights rather than peak areas should be used when tetryl is present in concentrations that are significant relative to the concentration of 2,4,6-TNT.

4.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

Samples are collected and handled as specified for semivolatile organics, (SW-846 Update IV, Chapter Four). Section 7.0 and table 6-1 and 6-2 of the Empirical Laboratories' Quality Assurance Manual include details concerning sample preservation, containers and handling of semi-volatile samples. Samples and sample extracts are stored in the dark at 4°C. Samples are stored in the sample storage walk-in cooler. Extracts are stored in the Hobart in the extraction laboratory. The holding time for samples is 7 days for waters and 14 days for soils. The holding time for extracts is 40 days.

5.0 INSTRUMENTATION, APPARATUS AND MATERIALS

5.1 Instrumentation

Agilent Series 1100 HPLC System

- Agilent G1311A Quaternary Pump
- Agilent G1379A Degasser
- Agilent 1313A 100 Position Autosampler
- Agilent G1316A Column Compartment
- Agilent G1314A Variable Wavelength Detector
- Agilent HPLC Chemstation

Hewlett Packard Series 1050 HPLC System

- Hewlett Packard Model 79852 1050 Quaternary HPLC Pump
- Hewlett Packard Model 79853 Variable Wavelength UV-VIS Detector
- Hewlett Packard 1050 79855A 21 Position Autosampler
- Hewlett Packard 1050 100 Position Autosampler Upgrade
- Hewlett Packard Model 79856A 1050 Solvent Module
- Hewlett Packard Model G1303A Vacuum Degassing Module
- Dell OptiPlex 933 GX150 Pentium III Computer
- Hewlett Packard PC Communication for HP Chemstation
- Hewlett Packard HPLC Chemstation
- SideWinder Temperature Control Module

5.2 Apparatus and Materials

- Solid-phase extraction system consisting of:
  - Manifold Station, *J.T. Baker spe-12G*, or equivalent
  - Tubing and connectors
  - SFE extraction cartridges, *Porapak®RDX Cartridges* or equivalent
  - Vacuum system capable of maintaining 18 inches of mercury
- Branson ultrasonic bath cooled by a chiller to 15-20°C
- Balance $\pm$ 0.01 g.
- Vortex mixer.
- Magnetic stirrer with stirring pellets.

- Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C).
- Disposable cartridge filters - 0.45 mm PTFE filter.
- Scintillation Vials - 20 mL, glass.
- Vials - 15 mL, glass, Teflon-lined cap.
- Vials - 40 mL, glass, Teflon-lined cap.
- Disposable syringes - Plastipak, 3 mL and 10 mL or equivalent.
- Volumetric flask with ground glass stopper - 100 mL and 1000 mL.
- Vacuum desiccator - Glass.
- Mortar and pestle - Steel.
- Sieve - 30 mesh.
- Graduated cylinders - 10 mL, 25 mL, 250 mL, 1000 mL.
- Pasteur pipet - length 9 ".
- Manual Sample Mill.
- Wiley Sample Mill.
- Clippers for cutting vegetation

6.0 REAGENTS AND SOLUTIONS

6.1 Reagents

- Acetonitrile, CH_3CN - HPLC grade.
- Methanol, CH_3OH - HPLC grade.
- Calcium chloride, $CaCl_2$ - Reagent grade. Prepare an aqueous solution of 5g/L. This is for use with soil/sediment samples.
- Sodium Chloride, NaCl - Reagent grade.
- Organic-free reagent water. Obtained from the Nano Pure Water System in the GC lab.
- 1% Acetic Acid, CH_3COOH, Solution – Prepare using 5.0mL CH_3COOH to 500mL of Organic free reagent water.
- Sodium Chloride solution - 325 g NaCl per 1000 mL reagent water.

6.2 Calibration/Method Standards

Stock standards are purchased in mixtures from reputable vendors. The date they are received is noted on the label and recorded in the Organic standards logbook. The date they are opened is noted on the label and recorded in the Organic standards logbook along with their lot number and vendor. Each standard that is prepared is recorded in the Organic standards logbook and given a sequential number. Each standards label is completed with the standard number, name, preparation date, expiration date, solvent and analyst initials. All standards are stored in the refrigerator in the dark at a temperature of 4°C ± 2°C or less from the date they are received/prepared. The refrigerator temperature is monitored daily with an annually calibrated thermometer and recorded with calibration correction in the GC refrigerator/freezer logbook or the Extraction temperature/calibration

logbook. Makeup of some common standards is detailed below. The makeup of other standards can be found in the Organic standards logbook.

- Calibration Solutions - The 8330 calibration standards are prepared as follows using solutions purchased from Restek or an equivalent vendor.

  Explosvie (Mix#1,#2 and Surrogate) Calibration Stock Solutions: Using a 100µL syringe, 100µL of Mix # 1, Mix # 2, and Surrogate (Restek at 1000 µg/mL) are injected into a 10mL volumetric flask containing approximately 9.5mL 1:1 acetonitril and water and diluted to volume with same to make a 10 µg/mL standard. After capping and inverting several times, the solution is transferred into a labeled, 12ml, teflon-lined, screw-capped vial and stored in the refrigerator in the dark at 4°C or less for up to six months. These standards are used to make the calibration curve standards in 1:1 acetonitrile and water at concentrations of 10, 5.0, 1.0, 0.50, 0.10 and 0.025 µg/mL. The lowest calibration standard can be extended down to 0.010µg/ml, if required.

  Mix # 3 Calibration Stock Solution: Using a 500µL syringe, 500µL of Mix # 3 (Restek PETN & Nitroglycerin, NG, at 1000 µg/mL) is injected into a 10mL volumetric flask containing approximately 9.0mL 1:1 acetonitrile and water and diluted to volume with same to make a 10 µg/mL standard. After capping and inverting several times, the solutions are transferred into a labeled, 12ml, teflon-lined, screw-capped vial and stored in the refrigerator in the dark at 4°C or less for up to six months. These standards are used to make the calibration curve standards in 1:1 acetonitrile and water at concentrations of 50, 25, 5, 2.5, 0.50 and 0.25 µg/mL.

- Matrix/LCS Spike Standard - The 8330 spiking solution is prepared by adding 0.5mL of a solution purchased from Ultra (Combined Stock Solution) in 50mL of acetonitrile for a final concentration of 10 µg/mL. Samples are spiked with 1 mL of this solution.

- Second Source Calibration Solution - The 8330 second source standard is prepared as follows using a solution purchased from Ultra(Combined Stock Solution) and Accustandard Inc.(Mix #3) or an equivalent vendor.

  Second Source Stock Solutions: Using a 100µL syringe, 100µL of Combined Stock Solution (Ultra at 1000 µg/mL) is injected into a 10mL volumetric flask containing approximately 9.5mL 1:1 acetonitrile and water and diluted to volume with same to make a 10 µg/mL standard. After capping and inverting several times, the solution is transferred into a labeled, 12ml, teflon-lined, screw-capped vial and stored in the refrigerator in the dark at 4°C or less for up to

six months. This standard is used to make a second source check standard 1:1 acetonitrile and water at 1.0 µg/mL.
Using a 500µL syringe, 500µL of Mix #3(Accustandard at 1000 µg/mL) is injected into a 10mL volumetric flask containing approximately 9.0mL 1:1 acetonitrile and water and diluted to volume with same to make a 10 µg/mL standard. After capping and inverting several times, the solution is transferred into a labeled, 12ml, teflon-lined, screw-capped vial and stored in the refrigerator in the dark at 4°C or less for up to six months. This standard is used to make a second source check standard 1:1 acetonitrile and water at 5.0 µg/mL.

- Surrogate Spike Solution- The 3,4-DNT solution (1-Chloro-3-Nitrobenzene may be used as an alternate) is prepared as follows using a standard purchased from Restek or an equivalent vendor.

  Surrogate Spiking Solution: Using a 250µL syringe, 200µL of 3,4-DNT, (or 1-Chloro-3-Nitrobenzene), (Restek at 1000 µg/mL) is injected into a 100mL volumetric flask containing approximately 95mL acetonitrile and diluted to volume with same to make a 2.0 µg/mL standard. After capping and inverting several times, the solution is transferred into several labeled, 40ml, teflon-lined, screw-capped vial and stored in the refrigerator in the dark at 4°C or less for up to six months. Samples are spiked with 1 mL of this solution.

7.0 PROCEDURE

All waters have a seven-day holding time and soils have a 14-day holding time. Determine the samples necessary to extract as follows:

- Each day a backlog report will be provided indicating sample numbers with the respective analysis required. Line through all the extractions that have been completed and plan to do the remaining analysis within the required holding time.

- Samples requiring RUSH turn around time may be logged in throughout the day which will require your immediate attention. Log-in personnel will generally communicate this need.

- Check with log-in throughout the day and examine the COC (chain of custody) forms that arrive with each set of samples. If an analysis is ongoing, extra QC may be avoided by picking up those extractions on the same day.

- Wearing lab coat, gloves and safety glasses, get samples from cooler. Samples must be signed out of the walk-in refrigerator. Enter the sample numbers, your initials and the date and time removed on the log provided. Inspect as to

whether they are in glass(soil)/glass amber jar(water) and have a Teflon lid. Find out if any special dilutions or screens need to be made for this client.

Before extraction, all glassware must be prepared as instructed in SOP-306 . Before weighing, the balance must be calibrated with ASTM Class I weights which bracket the amount to be weighed and recorded in the Extraction temperature/calibration logbook. If a heavy container is to be used for weighing, place a representative container on the balance, tare the balance and then calibrate the balance with the chosen weights. During extraction, all pertinent information (glassware, amounts, reagent lots, standards, etc.) is recorded in the HPLC 8330 extraction logbook so as to allow reconstruction of the extraction in the future.

7.1 Low Level Aqueous Sample Preparation Method (salting-out extraction)

- The extraction procedure for low-level waters should be read carefully and thoroughly before the extraction process is begun. Before extraction begins get out enough volumetric flask for each sample, method blank, laboratory control sample, matrix spike and matrix spike duplicate. Place an Avery label on each flask containing the following information: Lab #, Client name, Type of Analysis, Initial Volume - Final Volume, and the Lab Prep Batch Code. The lab prep batch code is defined as MMDDYYExLW# where #: 1 = 1st Method Blank for the day; 2 = 2nd Method Blank for the day; etc. The Method Blank and LCS label should include all lab #s in this set of samples.

- Add 251.3g of sodium chloride to a 1L volumetric flask. Measure 770 mL of a water sample using a 1L graduated cylinder and transfer it to the volumetric flask containing the salt. Add 1.0 mL of surrogate standard (2.0 µg/mL) using a 1.0 mL syringe to each sample, method blank and QC sample. Add 1.0 ml of 8330 standard spiking solution to each appropriate QC sample (LCS, MS&MSD).

- There are four Dynastir stir plates that were bought specifically to be used for this extraction. These stir plates have potentiometers on the bottom of them so the stir speed can be adjusted. They have initially been set so the highest speed will produce a good vortex. Add a stir bar to the flask containing the salt and sample and place on the stirrer. Stir until the salt is completely dissolved.

- Add 164 mL of acetonitrile while the solution is being stirred and stir for an additional 15 minutes. The acetonitrile should be added slowly. If the acetonitrile is added too fast the liquid level will rise to the top portion of the volumetric flask and poor mixing will result. This in turn results in acetonitrile recoveries much greater than 8 mL. Turn off the stirrer and allow the phases to separate for 10 minutes.

- Remove the acetonitrile (upper) layer with a pasteur pipet and transfer it to a 100 mL volumetric flask. Add 10 mL of fresh acetonitrile to the water sample in the 1 L flask. Again stir the contents of the flask for 15 minutes followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract. The inclusion of a few drops of salt water at this point is unimportant.

- Add 84 mL of salt water (325 g NaCl/1000 mL) to the acetonitrile extract in the 100 mL volumetric flask. Add a stir bar and stir the contents on a magnetic stirrer for 15 minutes followed by 10 minutes for phase separation. Carefully transfer the acetonitrile phase to a 10 mL graduated cylinder. At this stage the amount of water transferred with the acetonitrile must be minimized. Note: the water contains a high concentration of sodium chloride that produces a large peak at the beginning of the chromatogram where it could interfere with the HMX determination.

- Add an additional 1.0 mL of acetonitrile to the 100 mL volumetric flask. Again stir the contents of the flask for 15 minutes followed by 10 minutes for phase separation. Combine the second acetonitrile portion with the initial extract in the 10 mL graduated cylinder. Record the total volume of acetonitrile extract to the nearest 0.1 mL. (Use this as the volume of total extract [Vt] in the calculation of concentration after converting to mL). The resulting extract, about 5-6 mL, is then diluted 1:1 with reagent water prior to analysis.

- If the diluted extract is turbid, filter it through a 0.45 mm PTFE filter using a disposable syringe. Discard the first 0.5 mL of filtrate, and retain the remainder in a Teflon-capped vial for HPLC analysis.

7.2 High Level Aqueous Extraction Method

- Before extraction begins get out enough scintillation vials for each sample, method blank, laboratory control sample, matrix spike and matrix spike duplicate. Place an Avery label on each vial containing the following information: Lab #, Client name, Type of Analysis, Initial Volume - Final Volume, and the Lab Prep Batch Code. The lab prep batch code is defined as MMDDYYEW# where #: 1 = 1st Method Blank for the day; 2 = 2nd Method Blank for the day; etc. The Method Blank and LCS label should include all lab #s in this set of samples.

- Place a 5 mL aliquot of each water sample in an appropriately labeled scintillation vial and add 4 mL of acetonitrile (3 mL for MS/MSD samples). Add 1.0 mL of the surrogate standard (2.0 µg/mL) using a 1.0 mL syringe to each sample, method blank and QC sample. Add 1.0 ml of 8330 standard spiking solution to each appropriate QC sample (LCS,

MS&MSD). Shake samples thoroughly, and filter through a 0.45mm PTFE filter using a disposable syringe. Discard the first 3 mL of filtrate, and retain the remainder in a Teflon-capped vial for HPLC analysis. HMX quantitation can be improved with the use of methanol rather than acetonitrile for dilution before filtration.

7.3 Solid-Phase Extraction

This extraction method may not be appropriate for aqueous samples with greater than 1% suspended solids. Consult SW-846 Method 3535 for additional information.

- Mark the outside of the sample container at the sample meniscus with "white-out". This mark will be used to determine the initial sample volume after processing the contents. Add 1.0 mL of the surrogate standard (2.0 µg/mL) using a 1.0 mL syringe to each sample, method blank and QC sample. Add 1.0 ml of standard spiking solution to each appropriate QC sample (LCS, MS&MSD).

- Assemble the manifold for multiple extractions with SPE cartridges.

- Wash the cartridges with 10 mL acetonitrile and 30 mL reagent water with gravity flow, **do not let cartridge go dry. If it goes dry, you must start over.**

- Add sample to the cartridge and attach connectors and tubing.

- Turn on the vacuum pump and begin drawing sample through the cartridge, while adjusting the flow to 10mL/min.

- Empty the water trap as needed.

- After the sample extraction is complete draw air through the cartridge for 15 minutes to dry.

- Add 5 mL of acetonitrile to the cartridge and allow it to pass through with gravity flow collecting it in a 15 mL graduated tube. Note: the volume of acetonitrile may be reduced to 3ml to lower detection limits. Place an Avery label on each tube containing the following information: Lab #, Client name, Type of Analysis, Initial Volume - Final Volume, and the Lab Prep Batch Code. The lab prep batch code is defined as MMDDYYEW# where #: 1 = 1st Method Blank for the day; 2 = 2nd Method Blank for the day; etc. The Method Blank and LCS label should include all lab #s in this set of samples. Measure the final volume. Add as much calcium chloride solution to the final volume as was returned. Record this volume in the HPLC extraction logbook. The extract is ready for analysis, proceed to Section 8.0.

- Determine the original sample volume by refilling the sample bottle to the mark made with "white out". Transfer the liquid to a plastic 1000-mL graduated cylinder and record the sample volume in the HPLC extraction logbook to the nearest 10-mL. Transfer this information to the Avery label also.

7.4 Soil and Sediment Samples

Dry representative soil samples at room temperature, normally overnight, being careful not to expose the samples to direct sunlight. Grind and homogenize the dried sample thoroughly in an acetonitrile rinsed mortar so it will pass through a 30 mesh sieve. In other words, grind to a fine-dust like particle size. If one grinds the sample down to this small of a partical size, then the sieve would not be required.

NOTE : Soil samples may be screened by a commercially available test kit prior to grinding in a mortar and pestle. Visually observe the sample for lumps of material that have a chemical appearance. These lumps should be suspect and not ground. Explosives are generally a very finely ground grayish-white material. Soil samples as high as 2% 2,4,6-TNT have been safely ground. Samples containing higher concentrations should not be ground in the mortar and pestle. 2,4,6-TNT is the analyte most often detected in high concentration in soil samples.

Grinding of Vegetation Samples

Remove sample from shipping container and brush off dirt particles. Chop sample into about half inch pieces with clippers or other cutting tool. Place the sample in an aluminum pan and air-dry in an exhaust hood to the appropriate dryness for grinding. It should be dry enough where it won't stick to the inside of the mill. Grind the dried sample to fineness in either the manual sample mill or the Wiley mill or both if needed. Place the ground sample in a container and label immediately. Use 6g for extraction.

- Sample Extraction: Get out enough 40 mL vials for each sample, method blank and QC sample to be extracted. Place an Avery label on each vial containing the following information: Lab #, Client name, Type of Analysis, Initial Weight - Final Volume, and the Lab Prep Batch Code. The lab prep batch code is defined as MMDDYYES# where #: 1 = 1st Method Blank for the day; 2 = 2nd Method Blank for the day; etc. The Method Blank and LCS label should include all lab #s in this set of samples. Weigh-out a 2.0 – 2.3 g subsample of each soil (use a blank matrix soil for each method blank and LCS) into the appropriately labeled 40 mL vial. To each QC sample, (LCS, MS&MSD), add 8.0 mL of acetonitrile. Then add 1.0 mL of surrogate (2.0 µg/mL) standard and 1.0

ml of 8330 standard spiking solution. To each sample and method blank add 9.0 mL of acetonitrile and 1.0 mL of surrogate (2.0 µg/mL) standard using a 1.0 mL syringe. Cap each vial with a Teflon-lined cap and place in a cooled ultrasonic bath for 18 hours. The ultrasonic bath is cooled to ≤20°C. The temperature of the ultrasonic bath water is monitored at the beginning and the end of the sonication procedure. The temperature is recorded with calibration correction in the HPLC extraction logbook.

- After sonication, allow the sample to settle (10-15 minutes should be adequate). Add 10mL of calcium chloride and centrifuge samples for 10 minutes. (The calcium chloride solution is added to the samples to coagulate suspended particles and remove them from the supernatant.) Make sure the sample is labeled correctly.

8.0 HPLC ANALYSIS

8.1 Chromatographic Conditions

Agilent Series 1100 HPLC System

- Primary Column: C-18 reverse phase HPLC column, 25 cm x 4.6 mm, 5 µm.
- Mobile Phase: 57% methanol/43%water.
- Flow Rate: 1.0 ml/min.
- Injection Volume: 100 µL.
- UV Detector: 254 nm.
- Temperatrue: 28 degrees Celsius.

Hewlett Packard Series 1050 HPLC System

- Secondary Column: Phenyl-hexyl HPLC column, 25 cm x 4.6 mm, 5 µm.
- Mobile Phase: 39% acetonitrile/61%water.
- Flow Rate: 1.5 ml/min.
- Injection Volume: 100 µL.
- UV Detector: 254 nm.
- Temperatrue: 28 degrees Celsius.

8.2 Calibration of HPLC

- Upon initial startup of the pump, flow is increased to 5.0mL/min after opening the purge valve to bleed air from the solvent/water lines. When all air bubbles have been removed, the flow is reduced to normal run conditions and the purge valve is closed. The instrument is then pumped with 100% solvent for 45 minutes and then pumped with the appropriate solvent/water mixture for an additional 45 minutes.

- Initial Calibration: Injections of each calibration standard over the concentration range of interest are sequentially injected into the HPLC. Peak areas or heights are obtained for each analyte. (Peak height may be used instead of peak area for 2,4,6-TNT because degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak.) The calibration curve should be linear. However, some target analytes may be difficult to optimize without application of quadratic or higher order mathematical functions. Linearity may be determined using linear regression analysis for each target analyte by calculating the correlation coefficient *r*. Another term used to describe the goodness of fit of the line is coefficient of determination r^2 (the square correlation coefficient). The resulting line would normally not be forced through the origin or use the origin as a calibration point unless it is demonstrated that the intercept of the regression line is not statistically different from zero at 95% level of confidence. Linearity may be evaluated by calculating the percent relative standard deviation (*%RSD*). Alternatively the average response factor (*RF*) for each analyte may be used if the *%RSD* is less than 20%. Linearity is presumed if *r* is equal to or greater than 0.995, if r^2 is equal to or greater than 0.99 using six points. QC elements and acceptance limits are summarized in Table 1-8, pg. 22, taken from USACE *Appendix 1, Shell for Analytical Chemistry Requirements;* EM-200-1-3 2/01/01. Also found in Table B-2 of the *DoD Quality Systems Manual*, *Version 3*, January, 2006.
    - Due to the lack of resolution between 2-Am-DNT and 4-AM-DNT, calibration of these compounds can be based on "isomeric pairs". Improved resolution may be obtained using a Supelco C-18 column with eluent of 57%/43% (v/v) methanol and water at 1.0 mL/min.

  A visual inspection of the calibration curve should also be used as a diagnostic tool when nonlinear behavior is observed to verify if there is a large percentage error in any particular portion of the calibration curve. If the visual inspection indicates problems, or if one criteria is not met, then evaluate the following items for implementation based on an understanding of the detector response/contaminant concentration relationship.

    - Check the instrument operating conditions or the initial calibration standards used and make adjustments to achieve a linear calibration curve.
    - Narrow the calibration range using the same number of standards. Generally the highest standard is lowered first. The consequences of all actions taken must also be evaluated, i.e., reduction of the calibration range, raising of the Method Quantitation Limit, MQL, etc.
    - Evaluate the use of a nonlinear curve, when applicable. When nonlinear calibration models are used, the resultant line should not

be forced through the origin and the origin should not be used as a calibration point. No higher than a third-order (cubic) calibration model shall be used. When a nonlinear calibration model is employed, more data points are needed to maintain at least three degrees of freedom. For example, use of a quadratic function requires at least a six-point initial calibration curve. The resulting r^2 should be greater than or equal to 0.99 for this to be considered acceptable.

- Use of alternative techniques (e.g., relative standard error (RSE) outlined in the USEPA Memorandum, "Clarification Regarding Use of SW-846 Methods" (EPA/SW-846).

The standards used to make the calibration curve are verified to be accurate using a standard obtained from a second source, initial calibration verification (ICV). The percent recovery for the ICV target analytes determined from the initial calibration curve must agree within ± 15% (**80-120% DOD QSM Ver. 3**). If not, the source of the problem must be identified before analysis continues.

- Daily Calibration: Continuing calibration verification (CCV) standards must be analyzed, at a minimum, at the beginning of the day, after every 20 samples and at the end of the sequence(**at the beginning and end of sequence and after every 10 field samples, 20%D no average DOD QSM Ver.3**). The response factor for the CCV must agree within 15% of the response factor of the initial calibration. The same criteria is required for subsequent CCV responses compared to the response factor of the CCV beginning the day. If the CCV criteria are not met and a reanalysis does not meet, a new initial calibration curve may be needed. The same analyte limitations, as mentioned above for initial calibration, for certain compounds that make the stated method acceptance criteria unattainable are evaluated for percent differences, *%D*, for CCVs. Evaluate the mean of the *%D* or percent drift values for all reported target analytes in the calibration verification standard to verify whether it is less than the method acceptance criteria. To avoid the inclusion of target analytes showing gross method failure, this approach may be utilized as long as the target analytes do not exceed the criteria for poor performers in Table 1-8 pg. 22 (same as above). **In addition the client must be notified of all target analytes exceeding method acceptance criteria, the individual *%D* values for those compounds, and the mean *%D* calculated. DOD QSM Ver. 3 does not allow averaging for the CCV.**

8.3 RT Windows

Retention time (RT) windows are determined for each compound through the analysis of 3 standards over a 72 hour period. The standard deviation of the standard retention times is calculated and the RT windows are determined to be ± 3x this standard deviation. New in-house retention time windows are established after every major change to the system (new column or flow) and after a new initial calibration

using the mid-point standard. Retention times of each analyte in each CCV are compared to the established retention time window. Each analyte must fall within it's respective RT window. If this criterion is not met, the system must be adjusted to allow another CCV to meet criteria, or a new initial calibration performed and new retention time windows established.

8.4 Sample Analysis

- Samples will be prepared, analyzed and reported in batches and will be traceable to their respective batches. Quality control, QC, samples are required with each batch. A method blank, matrix spike/matrix spike duplicate and laboratory control sample is required for each sample matrix batch(normally sets of 20 samples). See section 9.0 for detail concerning the QC samples.
- Analyze the samples using the same conditions as the standards. Compounds identified on the C-18 column must be confirmed by injection on the Phenyl-hexyl column with an RPD limit of 40%. If the RPD exceeds 40%, results should be evaluated to determine if coelution or matrix is causing the exceedence and the reason noted. In cases of coelution or obvious matrix interference, the lower concentration may need to be reported. If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the higher result. Results should be flagged with a *'P'* on the report.
- Identification of a compound is made if a peak is found within the RT window on the C-18 column and then confirmed on the Phenyl-hexyl column. Column temperature control is employed so retention time shifts should not be a problem.

8.5 Data Reduction/Evaluation

- Each sample analysis sequence is documented in the HPLC run log. After the samples have been analyzed, the data is reduced using Target. All calculations are performed as covered in section 8.6 of this SOP. The following must be checked to determine if the sample will need any reanalysis or dilution:

  1. The initial CCV must be within $\pm$15 % difference of the calibration curve. Each CCV that follows must be within $\pm$15% difference of the calibration curve. Samples analyzed after a CCV which does not meet these criteria must be evaluated per section 8.2 and may require to be reanalyzed with a CCV which meets these criteria. See Table 1-8, pg. 22 (same as above). (**at the beginning and end of sequence and after every 10 field samples, 20%D no average DOD QSM Ver.3**)

2. Analyte concentration must be within the range of the calibration curve. If an analyte exceeds the curve, a dilution must be performed.

3. Surrogate recovery must be within the limits established by the laboratory or default values (USACE-Shell, Appendix 1; EM-200-1-3, 2/01/01.) of 60%-140% for water and 50-150% for solids/project sample matrix(**When analyzing samples for DOD QSM Ver. 3 projects, use DOD limits**). If the surrogate recovery falls outside the limits, the sample may need to be reextracted to verify matrix affect or the sample data must be qualified. See Table 1-8, pg. 22 (same as above).

- After the data has been reduced and determined to be acceptable, it is placed on a sample report and reviewed. Formal data evaluation is detailed in SOP-216 and documented using the USACE Analyst Data Review Checklist for USACE projects (example on pages 20 and 21).

8.6 Calculations

- Calculate the calibration factor for each analyte at each concentration as:

$$CF = \frac{\textit{Peak Area (or Height) of the Compound in the Standard}}{\textit{Mass of the Compound Injected (in nanograms)}}$$

- The mean CF is calculated as follows:

$$\overline{CF} = \frac{\sum_{i-1}^{n} CFi}{n}$$

- The standard deviation (SD) and the relative standard deviation (RSD) of the calibration factors for each analyte are calculated as follows:

$$SD = \sqrt{\frac{\sum_{i-1}^{n} (CFi - \overline{CF})^2}{n-1}}$$

$$RSD = \frac{SD}{\overline{CF}} \times 100$$

- Calibration verification involves the calculation of the percent drift (linear or quadratic) or the percent difference (average) of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference, depending on the calibration procedure used.

$$\% \text{ Drift} = \frac{(\text{Calculated concentration} - \text{Theoretical concentration}) * 100}{\text{Theoretical Concentration}}$$

where the calculated concentration is determined from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{(\text{CCV CF} - \text{Average CF}) * 100}{\text{Average CF}}$$

o External standard calibration - The concentration of each analyte in the sample may be determined by calculating the amount of standard injected, from the peak response, using the calibration curve. The concentration of a specific analyte is calculated as follows:

Aqueous Samples:

$$\text{Concentration } (\mu g/L) = [(A_S)(V_t)(D)]/[(\overline{CF})(V_i)(D)]$$

where:

A_S = Response for the analyte in the sample, units may be in area counts or peak height.

V_t = Total volume of the concentrated extract..

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1.

$\overline{CF}$ = Mean calibration factor from initial calibration (area/ng)

V_i = Volume of extract injected, µL.

V_S = Volume of aqueous sample extracted, mL.

Using the units specified here for these terms will result in concentration units of ng/mL, which is µg/L.

Nonaqueous Samples:

$$\text{Concentration } (\mu g/kg) = [(A_S)(V_t)(D)]/[(\overline{CF})(V_i)(W_s)]$$

where:

W_s = Weight of sample extracted, g. The wet weight or dry weight may be used, depending upon the specific applications of the data.

A_S, V_t, D, $\overline{CF}$ and V_i have the same definition as for aqueous samples.

9.0 QUALITY ASSURANCE/QUALITY CONTROL/CORRECTIVE ACTIONS

9.1 Surrogate - All samples and QC are spiked with the surrogate. Care must be taken with the surrogate 3,4-DNT to prevent coelution with TNT. If it is not possible to obtain adequate resolution between the surrogate and TNT, another surrogate should be chosen (example 1-Chloro-3-Nitrobenzene). The surrogate recoveries from method blanks,

LCS and samples are charted to generate control limits. Default limits (USACE-Shell Appendix 1; EM-200-1-3; 2/01/01) are set at 60-140% for water and 50-150% for solids/project sample matrix. Surrogate recoveries must be within these limits for all samples and QC or reextraction/reanalysis may be performed to verify matrix affect. If matrix affect is confirmed or it is decided not to reextract/reanalyze, a corrective action report must be completed and forwarded within the same shift in which the problem was discovered. Also, the data must be flagged for QC problems on the final report. See Table 1-8, pg. 22 (same as above).**DOD limits will be used for DOD QSM Ver. 3 projects.**

9.2 LCS Sample - The LCS is analyzed at the frequency required by the regulatory agency or client (every batch or 20 samples, whichever comes first, for USACE projects). To prepare the LCS, a blank is spiked with the calibration standards. The recoveries are charted to generate control charts and limits. The default limits (USACE-Shell Appendix 1; EM-200-1-3; 2/01/01) are 60-120% recovery for waters and soils if the generated limits are wider or if limits have not yet been generated. If the LCS compound has a recovery above the upper limit, but the same compound is not detected in any of the batch samples, no corrective action is required. For all other situations, the LCS should be reanalyzed for the failed analytes only. If the second analysis fails, all associated samples should be reextracted/reanalyzed for the failed analytes only. All recovery problems need to be addressed and steps taken to locate their source. **DOD limits will be used for DOD QSM Ver. 3 projects.**

9.3 Method Blanks - The concentration of all method target analytes must be below ½ of the method reporting limit, MRL (USACE-Shell, Appendix 1; EM-200-1-3, 2/01/01; threshold value below which a result is reported as non-detected), for each method target analyte. The first step of corrective action is to assess the effect on the samples. If an analyte is found only in the method blank, but not in any batch samples, no further corrective action may be necessary. Steps should be taken to find/reduce/eliminate the source of this contamination in the method blank. If an analyte is found in the method blank and some, or all, of the other batch samples, then corrective action is required. The source of contamination must be investigated and appropriate action taken and documented to find/reduce/eliminate the source of this contamination. The method blank, and any samples containing the same contaminant, would likely be reextracted/reanalyzed. If a contaminant is found in the method blank and the samples, the compound concentration must be flagged with a 'B' on the final report unless the concentration is greater than 10x that found in the method blank. In any case, a corrective action report must be completed and forwarded within the same shift in which the contaminant is found.

9.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Sample - 1 in 20 samples are spiked for a MS/MSD. MS/MSD recovery limits are set at 50-140% recovery with a maximum RPD of 50% for normal analytes and

60% for poor performers (See Table 1-8 pg. 22; same as above). Generally, batch control is not based on MS/MSD results unless general method failure is determined to be the problem. In that case, the samples and associated QC would be reanalyzed for the failed analytes only. MS data evaluation must include the consideration of the following factors. **DOD limits will be used for DOD QSM Ver. 3 projects.**

9.4.1 Sample matrix - If the sample is a soil, grab sample or sequentially collected water sample it may affect the %R and RPD of the MS/MSD. Corrective action must be taken in the form of reanalysis if a method problem is indicated.

9.4.2 Original sample concentration - If a spiked compound has a problem and the concentration of that compound in the original sample was two or more times the concentration of the spike, no further corrective action may be necessary other than the generation of a corrective action report to document the problem.

9.4.3 MS vs. MSD - If a spiked compound has a similar problem in the MS and the MSD which is not traceable to the execution of the method, no further corrective action may be necessary other than the generation of a corrective action report to document the problem as matrix effect.

9.4.4 Non-target Interference - The presence of significant non-target interference should be brought to the immediate attention of your supervisor who should discuss the problem with the client/project manager to determine the action to be taken.

9.4.5 Documentation of Capability (DOC) - Each analyst must perform a DOC to demonstrate proficiency with this method. See SOP-414 for guidance.

9.4.6 MDLs are performed annually or when there is a change in the method or MDL checks are analyzed quarterly per DOD QSM Ver.3. See SOP-414 for details.

10.0 HEALTH, SAFETY,WASTE MANAGEMENT AND POLLUTION PREVENTION

10.1 Standard precautionary measures used for handling other organic compounds should be sufficient for the safe handling of the analytes targeted by Method 8330A. The only extra caution that should be taken is when handling the analytical standard neat material for the explosives themselves and in rare cases where oil or waste samples are highly contaminated with the explosives. The HMX, RDX, Tetryl, and 2,4,6-TNT are explosives and the neat material should be handled carefully. Drying at ambient temperature requires several days. Do not dry at heated temperatures!

10.2 Care should be used in handling all samples. Safety glasses must be worn in the lab at all times. The use of blue nitrile gloves and lab coats is highly recommended.

10.3 Research into expected sample content and concentration should be done in order to be prepared for additional safety considerations. Generally, any samples which need special consideration have applicable notes on the sample logs.

10.4 MSDS sheets are available for all reagents and standards which have been purchased. These are located in the office next to the technical director.

10.5 Please see Waste Disposal SOP-405, for instruction of proper disposal of waste generated from this area. Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

ANALYST DATA REVIEW CHECKLIST

Sample Number(s):	
Batch Number(s):	
Method:	**8330**

QA/QC Item	Yes	No	NA	Second Level Review
A. Initial Calibration				
1. Does the curve consist of at least five Calibration Standards?				
2. Is the low RL standard in the calibration curve?				
3. Are the % RSDs within QC limits for all analytes?				
B. Second Source Verification				
1. Was the initial calibration curve verified by a second source calibration standard (ICV) and have QC criteria been met?				
C. Continuing Calibration				
1. Are the Continuing Calibration Verification (CCV) standards analyzed every 20 samples and at the end of the sequence?				
2. Are the % differences within QC limits for all analytes?				
D. Sample Analysis				
1. Are all sample holding times met?				
2. Was pH checked and recorded for all water samples?				
3. Are all samples with concentrations > the highest standard used for initial calibration diluted and reanalyzed?				
4. Are all compounds identified on the primary column confirmed on the secondary column?				
5. Are Surrogate recoveries within QC limits?				

ANALYST DATA REVIEW CHECKLIST
8330 (Explosives)

QA/QC Item	Yes	No	NA	Second Level Review
E. QC Samples				
1. Is the Method Blank extracted at the desired frequency and is its concentration for target analytes less than ½ the MRLs?				
2. Is the Laboratory Control Sample and its percent recovery within QC limits?				
3. Is the Matrix Spike/Matrix Spike Duplicate extracted at the desired frequency and is the percent recovery/RPD within QC limits?				
F. Others				
1. Are all nonconformances included and noted?				
2. Are all calculations checked at the minimum frequency?				
3. Did analyst initial/date the appropriate printouts and report sheets?				
4. Are all sample ID and units checked for transcription errors?				
5. Are all manual integrations checked by a second reviewer to verify why they were performed?				

Comments on any "No" response:

Analyst: _____ _____

Second Level Review: _____ _____

Table I-8

Summary of measurement quality objectives for Method 8330 Explosives (USACE – Shell 2/01)

QC Element	Target Analyte/Surrogate	Poor Performers/Sporadic Marginal Failures[1]
Initial Calibration (I.9.2.2.8)	Primary Evaluation: $r \geq 0.995$, RSD ≤ 20%, $r^2 \geq 0.990$ Alternative Evaluation: Mean %RSD for all target analytes ≤ 20% with maximum allowable restriction noted at right for individual analytes.	No allowance Alternative Evaluation: Maximum allowable %RSD for each individual target analyte ≤ 40%
ICV (I.9.3)	%Rec = 85% - 115%	No allowance
CCV (I.9.5/I.9.5.2)	Primary Evaluation: %Drift ± 15%, %D ± 15% Alternative Evaluation: Mean %Drift/%D for all target analytes ≤ 15%, with maximum allowable restriction noted at right for individual analytes.	**No allowance** Alternative Evaluation: Maximum allowable %Drift/%D for each individual target analyte is ± 30%
MB (I.10.2.1/I.11.4.1)	Target Analytes: Analytes < one-half MRL	Not applicable
LCS (I.10.2.2/I.11.4.2)	Water: %Rec = 60% - 120%[2] Solids: %Rec = 60% - 120%[2]	Sporadic Marginal Failures[1]: %Rec = 40% - 150%
MS (I.10.2.4/I.11.4.3/I.11.4.3.2)	%Rec = 50% - 140%[2]	Sporadic Marginal Failures[1]: %Rec = 40% - 150%
MSD/MD (I.10.2.2/I.11.4.4)	RPD ≤ 50%	RPD ≤ 60%
Surrogates (I.10.2.5/I.11.4.5)	Interference-Free Matrix: Water: %Rec = 60% - 140% Solids: %Rec = 50% - 150% Project Sample Matrix: %Rec = 50% - 150%	Not applicable
Target Analyte Confirmation (I.12.3)	RPD ≤ 40%	RPD ≤ 40%

[1] The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if between 7 to 15 explosives are reported from the high-performance liquid chromatography analysis, 1 SMF is allowed to the expanded criteria presented for the LCS. If greater than 15 explosives are reported, 2 SMFs are allowed for the LCS. If the MS includes only a subset of compounds, allow only 1 SMF for this QC element.

[2] Due to the tendancy for Tetryl to decompose, an expanded criteria may be applied at 45% -140% for both the water and soil matrices.

SOXHLET EXTRACTION -

BNA AND PEST/PCB

USING SW846 METHOD 3541

SOP NUMBER: SOP-329

REVISION NUMBER: 14

APPROVED BY:

SECTION MANAGER

QUALITY ASSURANCE OFFICER

EFFECTIVE DATE: 10/04/06

DATE OF LAST REVIEW: 10/04/06

BNA& Pesticide/PCB NON-AQUEOUS MATRIX
(Soxhlet Extraction)
USING SW846 METHODS 3541

I. SCOPE AND APPLICATION

1. This SOP describes the extraction of BNAs and pesticides/PCBs from soil, sediment, sludges and waste solids by an automated method (3541).

II. INTERFERENCES

1. Solvents, reagents, glassware, and other sample processing apparatus can add interferences to sample analysis. Method blanks must be extracted under the same conditions as samples to demonstrate freedom from interferences.
2. Phthalate esters commonly found in plastics can interfer with the analysis. Plastics should be avoided.
3. Soap residue can degrade certain analytes such as aldrin and heptachlor. Glassware should be solvent rinsed to avoid this problem.

III. APPARATUS AND MATERIALS

- Stainless steel spatula
- Soxtherm automated extractor unit-with 6 position condenser assemblies, internal plumbing, electronic components, stand alone controller unit and a copper collection tank for spent solvent
- o Soxtherm extraction beakers-54 x 130 mm, capacity approximately 125-175 mL
- Suitable thimble (33 mm diameter by 80 to 94 mm length cellulose or equivalent
- Drying Column (Chromatographic column) - 20mm I.D. x 300 mm
- Kuderna Danish (KD) flask - 500 mL
- Concentrator tube – 10-mL part of KD setup
- Snyder column - 3 ball, macro
- Plastic connectors - blue to assemble KD
- Water bath - heated, with concentric ring cover, capable of temperature control. The bath should be used in a hood.
- Boiling chips - Teflon
- Vial – 2-mL amber with Teflon-lined screw cap
- Vial – 12-mL clear with Teflon-lined screw cap
- Syringe - 1 mL, 500 µL
- Graduated cylinder - Glass, Class A, 100 mL
- Pasteur pipette - length 9" and 5-3/4"
- Pasteur pipette bulb
- Labels - Avery
- Ring stand - 3 prong

- Burette clamp - double
- Rings - large enough to hold KD setup
- Aluminum foil - heavy duty
- 10-mL disposable pipette
- Nitrogen tank - equipped with pressure regulator
- TurboVap Concentrator with 200 ml concentrator tubes
- Balance - capable of weighing to 0.1 grams.
- Aluminum pie pans for mixing samples
- Glass wool- Contaminant free.

IV. REAGENTS

- Sodium Sulfate (Na2SO4) - Granular, anhydrous, trace pure 10-60 mesh (purchased in bulk containers from Fisher # S415-10S or equivalent) placed in a Pyrex tray and heated at 400 C for a minimum of 4 hrs, removed and then cooled in open air in the extraction lab, placed in a 2.5kg glass amber jug and left at room temperature.

- Glass Wool - Silane Treated (purchased from Supelco #2-0410 or equivalent).

- Methylene Chloride **(Please read SOP-336 before handling this solvent in our laboratory.)** (Dichloromethane) - suitable for spectrophotometry and gas chromatography (Omnisolv #DX0831-1 or equivalent)

- Acetone - suitable for spectrophotometry and gas chromatography (Omnisolv AX0116-1 or equivalent)

- Hexane - suitable for spectrophotometry and gas chromatography (Omnisolv HX0298-1 or equivalent)

- Hexane/Acetone (1:1) (v/v) of the above reagent grades.

- Methylene Chloride/Acetone (1:1) (v/v) of the above reagent grades.

- Surrogate/Spike Solutions - Verify the amount of surrogate/spike to add to the sample prior to addition. It can change if a different detection limit is required or the volume of sample being analyzed changes or if the initial concentration of stock is different than that listed below:

    1. **BNA Surrogate** - The base neutral and acid surrogates are mixed together in one solution. This solution is prepared in methanol by making a dilution of stock purchased from a reputable vendor. Use 0.5 mL of this solution per 15g of non-aqueous sample. **(For low level PAHs use 50µl of the 100µg/mL BN Surrogate spiking solution.)**

2. **BNA Spiking Solution** - The base neutral and acid spiking solutions are mixed together in one solution. This solution is prepared in methanol by making a dilution of stock purchased from a reputable vendor with same compounds as for calibration. Use 0.5 mL of this solution per 15g of non-aqueous sample.**(For low level PAHs use 100µl of the 50µg/mL PAH spiking solution.)**
3. **TCMX/DCB (2,4,5,6-Tetrachloro-meta-xylene/Decachlorobiphenyl)Warm and sonicate** - Surrogate solution is prepared in acetone by making a cut on stock purchased from a reputable vendor. 0.5 mL at 0.5 µg/mL of this solution is added per 15g of non-aqueous sample.
4. **PCB Spiking Solution-** Arochlor 1016/1260 or the PCB of choice (1242, 1248, 1254, or 1260 are the most common) is prepared in acetone at a concentration of 10 ppm. PCB stock is usually purchased from RESTEK or equivalent. The PCB to use may be determined by viewing historical data or asking the GC operator. Use 0.5 mL per 15.0 grams of non-aqueous sample.

5. **Pesticide Spiking Solution** - A spiking solution is prepared at 100 ug/L. Use 0.5 mL per grams of non-aqueous sample.

V. SAMPLE COLLECTION, PRESERVATION, AND HOLDING TIMES

1. Samples are collected in an appropriate size wide-mouth glass jar (4oz. or 8 oz.) with a teflon-lined cap.
2. Samples are preserved by cooling to 4° C.
3. Holding time is 14 days from collection date to extraction.

VI. PROCEDURE

Extraction Procedure

1. All soils have a 14 day holding time counted from the day they are sampled. (Exception: samples for **Hercules in New York have a 7 day holding time**). Determine the samples necessary to extract using the following information (DO NOT extract samples for which you have no information.):
   - Each day a backlog report will be provided indicating sample numbers with the respective analysis required. Line through all the extractions that have been completed and plan to do the remaining analysis within the required holding time.
   - Samples requiring RUSH turn around time may be logged in throughout the day which will require your immediate attention. Log-in personnel will generally communicate this need.
   - Check with log-in throughout the day and examine the COC (chain of custody) forms that arrive with each set of samples. If an analysis is ongoing, extra QC may be avoided by picking up those extractions on the same day.

2. Wearing lab coat, gloves and safety glasses, get samples from cooler. Samples must be signed out of the walk-in refrigerator. Enter the sample numbers, your initials and the date and time removed on the log provided. Inspect as to whether they are in glass and have a Teflon lid. Find out if any special dilutions need to be made for this client. If the sample has a particularly bad matrix or a strange matrix, see your supervisor to find out if a soxhlet extraction is truly necessary.

3. Get twice the number of aluminum pie pans to prepare the number of samples you have plus any additional spikes or LCSs and a method blank. A method blank and LCS must be processed with each set of samples. A matrix spike, a duplicate or a matrix spike duplicate and a LCS must be processed for each analytical batch (up to a maximum of 20 samples). Make an Avery label for each extract containing the following information: Lab #, Client name, Type of Analysis, Initial Weight - Final Volume, and the Lab prep batch code. The lab prep batch code for BNAs is defined as MMDDYYBs# where #: 1 = 1st method blank of the day; 2 = 2nd method blank of the day; etc. The lab prep batch code for Pest/PCBs is defined as MMDDYYPs# using the same logic. The Method Blank and LCS labels must include all lab #s in this set of samples.

4. Decant and discard any water layer on a sediment sample by carefully pouring this off into a trashcan.

5. Dump the entire sample into an aluminum pie pan and mix sample thoroughly with a spatula until mixture is homogenous. Discard any foreign objects such as sticks, leaves, and rocks.

   It is extremely important that waste (when appropriate), soil and sediment samples be mixed thoroughly to ensure that the sample is as representative as possible of the sample media. The most common method of mixing is referred to as quartering. The quartering procedure should be performed as follows:

   - *The material in the sample pan(inorganic-plastic/organic-aluminum) should be divided into quarters and each quarter should be mixed individually.*
   - *Two quarters should then be mixed to form halves.*
   - *The two halves should be mixed to form a homogenous matrix.*

   This procedure should be repeated several times until the sample is adequately mixed.

NOTE: Samples that are clay type materials should be handled in a different manner. Due to these type sample matrices having an affinity to stick to most anything that touches it, another approach must be followed. Obtain a representative sub-sample aliquot from the center or middle section of the sample container

6. Place an aluminum pie pan on the balance and zero it. Calibrate balance with ASTM class-1 Troemner weights or equivalent, bracketing desired weight (50g, 20g, 10g, 5g, 1g). Record

calibration in the Extraction calibration/temperature logbook. Using a spatula, transfer the **appropriate weight, {10-20 grams depending upon client or project specific Detection Limits (DL) and/or Reporting Limits (RL)}**, of a representative sample to the nearest 0.1 gram. Normally 10 or 15 gram sample weights are used. Record this amount on your label. Put your label on the side of the 400-mL beaker. For spiking purposes, weigh 3 aliquots of the appropriate sample. Pick a sample with a good matrix, one that mixes well, non-oily, etc.

7. Add ~ 20 grams of sodium sulfate to the aluminum pie pan. Using a spatula and/or a glass rod, mix the sample thoroughly with the sodium sulfate until it becomes a sandy texture. If necessary, add additional sodium sulfate. When removing the spatula or glass rod from the mixed sample, leave behind all the sample possible. Cover the aluminum pie pan with foil and continue to weigh up the remaining samples. For the method blank and LCS, simply weigh up 15 grams of sodium sulfate. The matrix used for the method blank and LCS must be free of the analytes of interest and processed through the same analytical steps as the samples.

8. Transfer the sample and its label to a soxtherm beaker, which has been prepared using a glass rod to place glass wool in and over the hole at the bottom side.

9. Make up 1:1 Methylene Chloride/Acetone (**for BNAs**) or 1:1 Hexane/Acetone (**for Pest/PCBs**) by mixing 2000ml of methylene chloride or hexane with 2000 ml of acetone in a 4000ml amber jug. Add 120 mL of this mixture to the soxtherm beaker for each sample, method blank, and spike - add boiling chips.

10. Verify the amount of surrogate/spike to add to the sample prior to addition. It can change if a different detection limit is required or the volume of sample being analyzed changes. Set out the surrogate/spike at least ten minutes before use to allow it to warm to room temperature. Someone must verify that the surrogate/spike has been added by placing a check mark on the label as it is added. NOTE: Be sure to invert syringe and eliminate air bubble when obtaining surrogate solution and spiking solution.

    NOTE: Surrogate and spike should be added just prior to setting the soxhlet apparatus on the hot plate(manual extraction) or hot block(automated extraction).

    Using the 1-mL glass syringe designated for BNA surrogate, add 0.5 mL of BNA surrogate to each sample, spike, and blank. **(For low level PAHs use 50µl of the 100µg/mL BN Surrogate spiking solution.)OR** using the 1.0-mL glass syringe marked TCMX/DCB surrogate, add 0.5 mL of TCMX/DCB surrogate to each sample, blank and spike.

    For the BNA sample in each analytical batch selected for spiking, use the 1.0-mL glass syringe marked Base Neutral Acid Spiking to add 0.5 mL (2.0 mL for CLP samples or samples known to require GPC cleanup) of the Base Neutral Acid Spiking solution. . **(For low level PAHs use 100µl of the 50µg/mL PAH spiking solution.)**

For Pest/PCB samples, determine if the sample will require a Pesticide Spike and/or a PCB Spike. Proceed as follows:

Pesticide and PCB - set up two LCS's – one for Pesticide getting a MIX A&B spike and one for PCB which should be spiked with PCB 1660. In addition to the LCSs, a matrix spike/matrix spike duplicate is only necessary for the pesticide. Don't do a PCB matrix spike.

Pesticide only – To the sample in each analytical batch selected for spiking, add 0.5 mL of Pesticide Spike (Mix A&B) with a glass syringe dedicated for Pesticide Spike.

PCB only - To the sample in each analytical batch selected for spiking, add 0.5 mL of PCB 1016/1260 (unless otherwise specified, 1248 for BB&L) using a 1.0 mL glass syringe dedicated to that PCB. Add 20 grams of Na_2SO_4.

NOTE: 0.5 mL of spiking solutions is required for *Soxtherm* automated soxhlet extraction because the final volume of these samples is 5.0 mL(the final volume for CLP samples or GPC cleaned samples is 2.5 mL). Use 1.0 ml Pesticide and PCB solutions for 3540C.

11. **Automated Soxhlet:** The *Soxtherm* will extract any number of samples up to six per run. Generally, we set up to complete four sets of six a day or/as sample load permits with required QC. Each extraction cycle takes 1-2 hours. Reference *O.I. Analytical Operator's Manual* for programming and making adjustments to extraction cycle settings.

- The extraction thimbles are placed into the respective extraction thimble holders(the open end of the thimble is nearly flush with the upper edge of the metal ring. Transfer the sample into the extraction thimble. The appropriate spiking solution should be added at this point (surrogates, MS/MSD or LCS etc...). (Placing a small piece of glass wool sufficient to cover the diameter of the thimble will help hold the sample mixture in the thimble.)

- Place 1-2 boiling chips in each extraction beaker and place each extraction thimble into the appropriate labeled beaker then add 120 mLs of the appropriate extraction solvent. (1:1 Acetone/Hexane for Pest/PCBs **or** 1:1 Acetone/Methylene Chloride for BNAs.)

- For loading samples to the *Soxtherm* the condensers should be in their raised position. If Viton gaskets are to be used, install them in the extraction beakers so that a good seal will form between the extraction beaker and the Teflon extraction cylinder. Install the extraction beakers by depressing the holding clamp and carefully sliding the beaker onto or off the bottom of the Teflon fitting that is situated below the glass condenser. After the extraction beakers containing the samples have been loaded on the *Soxtherm,* push all beakers against the rear limit stop of the hot plate.

- The *Soxtherm* is now ready to run with one of the programs listed below (**remember to check the sight glass on the front of the Extraction Unit to see if the solvent collection tank is near full and should be drained**).

Pest/PCB Extraction Program

Temperature	= 165°C (Maximum temperature 200°C)
Boiling Time	= 30 minutes
Solution Reduction A	= 5x15 ml
Extraction Time	= 30 minutes
Solution Reduction B	= 0 minutes
Solution Cooling	= 0 minutes
Solution Reduction Interval	= 2.5 minutes
Solution Reduction Pulse	= 2 seconds

BNA Extraction Program

Temperature	= 160°C (Maximum temperature 200°C)
Boiling Time	= 30 minutes
Solution Reduction A	= 5x15ml
Extraction Temperature	= 30 minutes
Solution Reduction B	= 0 minutes
Solution Cooling	= 0 minutes
Solution Reduction Interval	= 2.5 minutes
Solution Reduction Pulse	= 2 seconds

- At the end of Solution Cooling time the condensers and extraction beaker assemblies are automatically raised off the heating block and the process completion message appears on the display. Remove the beakers to a hood and continue with the process as listed below.

13. Enter the following information in the BNA, Pesticide and/or PCB extractions logbook: Client name, Lab #, date extracted, initial weight, final volume, soxtherm position, and anything unusual that may have occurred with this sample. Enter the ID# of the surrogate and spike used and the initials of the person that verified their addition to the sample in the appropriate logbook. Also record the vendor and lot number of the methylene chloride or hexane and acetone used.

14. Dry the sample by either of the following methods:

14A. Get a ring stand with a double burette clamp attached to it. Cover the burette clamp ends with aluminum foil to prevent the possibility of solvent touching the plastic coated ends and dripping into the extract. Place a drying column into the burette clamp and transfer a small amount of glass wool to the top of it. Tamp it to the bottom with a glass rod so that it adequately covers the hole at the bottom. Add approximately 10 cm of Sodium Sulfate to the column. Rinse with 20 to 30 mL of methylene chloride or hexane and discard this rinse into the appropriate waste container (make certain that methylene chloride waste goes in the chlorinated solvent waste container in the hood).

14B. Set up a ring stand with funnels. Place a small amount of glass wool in the bottom of it. Add ~2" sodium sulfate to the column and rinse with 20-30 mL methylene chloride or hexane for Pest/PCBs. Discard this rinse.

15. Two methods may be used for concentration-STEAM BATH or TURBO-VAP. **(BNAs are generally concentrated by the steambath method due to resulting low BN recoveries and formation of aldol condensation products when done by the Turbo-Vap method.) BNAs and Pest/PCBs have an additional 50 mLs of the appropriate solvent(hexane-Pest/PCBs; methylene chloride-BNAs) added to the sample during concentration to insure that the sample is in the correct solvent when it concentrates to final volume. The addition of the extra solvent also reduces aldol condensation products in the sample concentrate.** Pest/PCBs are generally done by the TURBO-VAP method. If you are using the TURBO-VAP concentration, proceed to 15B.

15A. STEAMBATH CONCENTRATION

A. Turn on the steam bath and the Kontes heater well before they are needed to insure that they are at proper temperature. The setting should be set (between 5 and 6 which yields a temperature around 80 to 90°C) for BNA extractions. A higher temperature could cause some of the compounds to be destroyed. Insure that there is enough water in the bath. (Water should cover the coils and be at approximately 1/4 inch below the surface of the overflow device.)

B. Rinse a Kuderna Danish flask and a concentrator tube with methylene chloride or hexane (for Pest/PCBs) and assemble together with a blue clip. Set this in the ring stand so that it will collect the extract as it passes through the funnel. Add a boiling chip to each KD setup. Pour the entire extract through the dry column/funnel. Rinse the 400 mL beaker, twice, with 10-20 mLs of methylene chloride or hexane (for Pest/PCBs) transferring the rinse to the funnel each time. Finally rinse the funnel with ~ 10 mLs of methylene chloride or hexane (for Pest/PCBs). Record the numbers of the Kuderna Danish, and the concentrator tube in the BNA or Pest/PCB logbook.

C. Slip a 3 ball Snyder column into the Kuderna Danish flask and set it on the water bath so that the concentrator tube is immersed in the hot water. Rinse the 3 ball Snyder with ~ 1 to 2 mLs methylene chloride(for BNAs) or hexane (for Pest/PCBs) into the KD. As the extract gets hot, the balls will begin to chatter, but the chambers should not flood with condensed solvent. The extract will evaporate in approximately 15 to 20 minutes. Monitor the evaporation of the solvent.

D. When you can no longer see it boiling above the surface of the bath, you need to keep a close vigil on the sample. Take it from the bath momentarily and check the level of extract in the concentrator tube. Don't allow it to quit boiling before placing it back into the water. When it reaches approximately 1/2 the length of the tube or 5 mL, remove it from the bath, set it in a ring on the ring stand and allow it to cool.

E. Remove the 3 ball Snyder and rinse down the sides of the flask with 1 to 2 mL of methylene chloride for a BNA or hexane for a Pest/PCB. Dry the union with a paper towel to remove excess water and prevent contamination. Disassemble the KD apparatus being careful not to loose any extract from the concentrator tube. Transfer the extract with rinses to a turbovap tube to concentrate further as for TurboVAP completion.

Concentration Problems:

- Oily, tarry extracts may be particularly difficult to concentrate to the 0.8 mLs required for a BNA extract. As the extract begins to concentrate, these extracts are usually very dark in color and leave residue on the sides of the 15 mL tube as they concentrate. When the extract has been in the heater a reasonable amount of time and will not concentrate to ~0.8 mL, remove the extract from the heater. Transfer to a suitable container. Measure and record the final volume in the extraction log and on the label. Further cleanup may be required on these samples. Coordinate this action with your supervisor.

15B. TURBO-VAP CONCENTRATION

A. Turn on the TurboVap and set the temperature at 40°C -50°C. This temperature is necessary to evaporate the acetone. Adjust pressure of nitrogen gas tank to >30 psi. Make sure the tank has 200 psi or more on the main valve.

B. Rinse a Turbo-Vap tube and arrange it underneath a rinsed, packed drying column/funnel. Pour the extract through the column/funnel so that it will collect in the tube. Total volume in the glass evaporator tube should not exceed 200 mLs to avoid splattering on the lid of the Turbo-Vap. Therefore the process cannot be completed in one step. Pour enough of the extract from the 400 mL beaker to reach the 200 mL level mark on the Turbo-Vap tube. To help prevent cross contamination, cover the turbovap tube with aluminum foil and punch a small hole in the top of it. A portion of the extract will remain in the beaker. This should be set aside with the funnel used to dry the first portion of the sample placed in the mouth of the beaker.

C. Record the Turbo-Vap tube number, the vendor and lot number of hexane used in the appropriate extraction logbook.

D. Place the glass evaporator tube in the Turbo-Vap. Be sure to push tube down so the tip slides into the sensor well. Close the lid to start concentration. Check that each position with a tube has an orange light showing. If the orange light is not steady, bubbles may be in the sensor and need removal. (See Turbo-Vap manual).

E. When the extract has been concentrated to ~1.0 mL, remove it from the Turbo-Vap and find the remaining extract. Reuse the original funnel and pour the remaining extract through it so that it drains into the turbovap tube. Rinse the 400 mL beaker

twice with 10 -20 mLs of methylene chloride or hexane for Pest/PCBs transferring the rinse to the funnel each time. Finally rinse the funnel with ~ 10 mLs of solvent. Place a piece of aluminum foil over the tube and with a sharpie mark an "X" on the aluminum foil. Remove the tube to a metal holder. Concentrate as before.

F. When the beep sounds indicating the end of concentration, the extract will be at approximately one half mL, remove the tube from the bath. The extracts are ready to be transferred into their appropriate vials.

- **For Pest/PCB Completion:** Hold the tube and the sample vial in one hand at about a 45° angle. Use a 9" pasteur pipette to draw up the sample and transfer it to the 10 mL vial. Be careful not to spill any sample during the transfer because one drop represents 5% of the sample and is a critical loss.
- Fill a 10 mL graduated cylinder with 9.5 mL of hexane. Add 1/2 of the hexane to the tube. Draw into the pipette and rinse down the conical portion of the tube several times. Transfer this rinse to the 10 mL vial. Add the remaining hexane and repeat this rinsing process. Cover the extract with a Teflon-sealed screw cap.

- **BNA Completion:** When the volume has been reduced to 1-0.5(~0.4)mL, remove the tube from the Turbo-Vap and place in a metal holder.
- Use a 9" Pasteur pipette to transfer the extract to a 2 mL amber vial. THIS IS THE MOST CRITICAL PART OF THE ENTIRE OPERATION!!! A single drop represents about 10 percent of the total sample. Before you move the tip of the pipette from the tube to the vial, be sure that a drop will not form on the end and fall off.
- Draw ~0.20 mL of methylene chloride into a 0.50 mL syringe and add ~ half of this aliquot to the tube. Draw the methylene chloride into a pipette and rinse the sides of the tube several times. Transfer this rinse to the 2 mL vial. Add methylene chloride from the syringe and repeat the rinsing process until you have ~ 1 mL in the sample extract vial.
- Compare this volume to a 2 mL dummy vial containing 1 mL of solvent to insure that you have not exceeded 1 mL. For low level PAHs the final volume is 0.5mL. The methylene chloride rinse volume must be adjusted to achieve this final volume. Compare the volume to a 2mL dummy vial containing 0.5 mL of solvent to insure that you have not exceeded 0.5 mL. The GC/MS operator will adjust the sample to the desired final volume and add internal standard just prior to analyses. Cover the extract with a Teflon-sealed screw cap and transfer the label to the vial.

NOTE: If the final extract is yellow or dark in color or the matrix is oily and viscous, further cleanup may be desired. Refer to SOPs 307 to 309 and 330 to 334 for further cleanup information. Discuss cleanup possibilities with the analyst and/or your supervisor.

The extract obtained above may now be analyzed. Refrigerate at 4°C or carry directly to the analyst. Samples must be signed into the Sample Extract refrigerator. On log provided, enter the sample numbers, your initials, and the date and time the samples were placed into the refrigerator.

16. **Documentation of Capability (DOC)**

Each analyst must perform a DOC to demonstrate proficiency with this method. Refer to SOP-413 for guidance.

17. **Waste Management and Pollution Prevention**

Please see Waste Disposal SOP-405 for the proper disposal of waste generated from this area.

Quantity of chemicals purchased should be based on expected usage during its shelf-life and the disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

18. **Method Performance**

Refer to SOP-201 and SOP-211 for method performance.

DEFINITIONS

BNA - Base/ Neutral/Acid
°C - degrees centigrade
COC - chain of custody
DL - detection limit
g - grams
KD - kuderna danish
LCS - laboratory control sample
•g/L - micrograms per liter
µL - microliter
•g/ml - micrograms per milliliter
ml - milliliter
mm - millimeter
MS - matrix spike
MSD - matrix spike duplicate
PAH - polynuclear aromatic hydrocarbons
PCBs - polychlorinated biphenyls
Pest - pesticides
RL - reporting limit
SOP - standard operating procedure
TCMX - tetrachloro-m-xylene
v/v - volume to volume

Refer to SOP-431 for further definitions

LABORATORY SAMPLE RECEIVING, LOG IN AND STORAGE STANDARD OPERATING PROCEDURES

SOP NUMBER: SOP-404

REVISION NUMBER: 10

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 07/20/06

DATE OF LAST REVIEW : 07/20/06

LABORATORY SAMPLE RECEIVING, LOG IN AND STORAGE

This SOP lists in as much detail as possible our daily procedures for sample receiving, log in and storage of laboratory samples. Keep in mind that there may be project specific requirements that are more strict or different than our routine procedures. In these instances, the project specific requirements must be met and followed. Although a few project specific requirements are detailed in this SOP, i.e. USACE certification issues, not every situation can be addressed. If there is ever any uncertainty on what procedures must be followed, please see the Testing Coordinator immediately. If ever in doubt, always go with the more stringent requirements. This document will constantly be reviewed and revised as necessary.

SAMPLE ACCEPTANCE CRITERIA

A sample should be rejected for compliance purposes if it does not meet the following criteria. Analyses may only proceed after notification and approval to proceed from the client.

1. Sample must be properly preserved and in the proper container for the requested analysis.
2. Sample integrity must be maintained. The container shall be intact without cracks, leaks, or broken seals.
3. Adequate sample volume must be received for the requested analysis, including volume for any necessary QA/QC (MS/MSD).
4. The sample ID on the bottle label must match the sample ID listed on the chain of custody.
5. The sample container label and the chain of custody must be completed with indelible ink. The sample label must be intact and list all necessary information; to include: sample date, sample time, sampler, and sample ID/location. The chain of custody shall also indicate sample date and time, requested analyses, and all necessary client information.
6. Sample temperature must be less than 6°C.
7. Sample must be within holding time for the requested analysis.

These issues are discussed in more detail below under the "Sample Receiving" section of this document.

I. Sample Receiving

A. Samples are received at the Empirical Laboratories on French Landing Drive in Nashville, TN.

1. The majority of samples are shipped in coolers by couriers such as Federal Express and UPS. All couriers are generally received in the Empirical Laboratories Sample Receiving (SR) area on the fifth floor. The laboratory is located close to the Federal Express (FedEx) distribution station, therefore we often pick up our coolers at the FedEx location and transport them back directly to the laboratory. Some coolers and/or samples are delivered directly to the SR area by the sampler and/or client.

2. Some coolers and/or samples may be received directly by Empirical Laboratories Sample Receiving personnel. If samples are hand delivered by the client make sure that necessary paperwork is included and that you sign and date the chain of custody. If the *ELAB of Tennessee* ***Chain of Custody [Attachment II]*** is used the white and yellow copy of the chain of custody is retained and the pink copy must be given to the client.

B. When going through the required steps for Sample Receiving and Sample Log In, keep in mind that a ***Corrective Action Report (CAR) for Sample Receiving [Attachment III]*** must be completed to document any problems, discrepancies, project changes, etc. encountered during the process. This includes but is not limited to incorrect sample containers, improper preservatives [chemical and temperature], chain of custody discrepancies, sample descriptions, etc. A CAR may be completed just to keep a record of a situation, which is not actually "out of compliance."

1. Make sure that all information on the CAR is stated clearly and very detailed. Many times it is necessary to refer to these documents a year or more after they were completed. Document all correspondence including name, date, company and response.

2. The CAR forms must be numbered starting with No. 001 at the beginning of the year (e.g. 01-001). No two forms should have the same number. All CARs must be forwarded to the Project Manager and/or receiving manager for approval and distribution. THIS MUST BE DONE ASAP OF WHEN THE PROBLEM/SITUATION IS DISCOVERED.

C. Visually inspect all coolers for tampering, custody seals present and intact (if applicable) leakage, etc. If a cooler has been damaged, unpack the samples and discard the cooler as to not reuse it. If you suspect a cooler may be damaged or is extremely dirty this cooler must not be reused. If coolers were sent by Federal Express, examine the Federal Express airbills for the number of packages in the shipment and make sure that all the packages (coolers, boxes etc.) in a group have been received. If there are any problems the Project Manager must be contacted immediately. If anything looks unusual, take the time to check it out and document the situation and findings.

D. Open each cooler in order to quickly inspect the contents and to locate the chain of custody. Sample Receiving personnel must wear the following personal protection equipment: gloves, safety glasses and a laboratory coat. All coolers received from projects with the US Army Corps of Engineering (USACE) projects should be opened under the hood in the sample storage room. Sign, and list the date and time received on the chain of custody. The time received must reflect the actual time the samples were received even though they may be logged into the system at a later time. Samples received on Saturday may be processed on the following Monday morning, or samples received late in the day during the week may be processed the next morning. All cooler(s) must be opened, examined for leakage, breakage etc., the temperature measured and the chain of custody signed and dated to reflect the actual date and time which they were received. The samples must be put in cold storage as soon as possible.

1. Attach any shipping receipts, work orders, etc. to the chain of custody.

2. If a chain of custody or other paperwork is not sent, the client must be contacted and the samples temporarily placed on hold in cold storage. In some instances the log-in person may complete a chain of custody. The required information may be found on the sample containers or it may be necessary to call the client to get the missing information (i.e. sample ID, collection date and time, etc.). Note on the chain of custody that it was completed by laboratory personnel and record the name of the person with whom you spoke. All attempts to encourage our customers to complete a chain of custody or submit written information for samples must be made.

3. Project specific paperwork may be required. For all USACE and USCLP projects, a ***Cooler Receipt Form [Attachment IV]*** must be completed for each cooler received. Sample receiving personnel must begin completing this form as soon as a cooler is received and complete this form as samples go through the log in process.

E. The temperature of each cooler or set of samples must be measured as quickly as possible using a thermometer with 0.1°C increments. This thermometer must be calibrated against a NIST certified thermometer once a year and this information recorded in a bound notebook. The Certificate of Calibration for the NIST thermometer is kept on file at the QAO's desk. The thermometer must be tagged with the unique identification number of SR#1; (Sample Receiving #1), the date calibrated and the correction factor. This information must also be recorded in a bound notebook. Only this thermometer can be used for recording the temperature of sample coolers upon receipt.

1. To measure the temperature, open the temperature control blank, point the IR thermometer at the liquid surface, wait 30 seconds for temperature to stabilize. Read the temperature to the nearest 0.1 °C. The corrected value temperature must also be recorded on the chain of custody. (This value will also be recorded into the LIMS at a later point.). All regulatory compliance samples received from North Carolina that do not meet the temperature requirement will be segregated and the North Carolina State Laboratory will be notified of the non-compliance (919-733-3908). The samples will not be logged in or analyzed until written notification is received from the State of North Carolina to proceed with analyses.

2. If a cooler is received with no temperature control blank bottle, pour up a small aliquot of sample from one of the sample containers (unpreserved if available) in the cooler and measure this as the temperature control sample. Discard this aliquot after the reading. If only VOA vials are received check with the Project Manager or Section Manager before opening any of the vials. If any sample is taken from the VOA vial for temperature measurement, the entire vial must be discarded. If non-aqueous samples are received without a temperature control blank then the temperature of the cooler itself can be monitored by placing the thermometer directly in the cooler. This should be noted.

3. If the temperature exceeds 6°C for any sample, the Project Manager or Sample Receiving personnel must contact the client immediately. There may be tighter temperature control limits for specific project requirements. The customer must make the decision to either continue with the analyses or resample. Make sure the client is aware that if the samples are analyzed, the following qualifier is normally included on the final report: "The shipping cooler temperature exceeded 6°C upon receipt to Empirical Laboratories. This may have an impact on the analytical results. The concentration may be considered as estimated." Not all samples for the project will be flagged, just those samples received above 6°C.

   Many times we are not able to get in touch with the client quickly and the best judgment on how to handle the samples must be made after discussion with the Testing Coordinator and/or Laboratory Director or Technical Director. The samples may still need to go through the log in process although it may be eventually determined that the samples will not be analyzed or the samples may temporarily be placed on hold and not logged in. Above all do not allow the samples to set out at room temperature for an extended period of time while waiting for a decision. **A CAR outlining the problem and all correspondence must be completed.**

   The only exceptions to the 6°C rule are:

   a. Water samples for all Metals, (except Chrome 6+) that have been preserved with HNO_3 to a pH of ≤ 2. *Keep in mind that non-aqueous sample for Metals must be cooled.*

   b. Samples for Fluoride, Chloride and Bromide.

   c. Waste/Product samples for all parameters.

   d. Samples generated in the Aquatic Toxicology laboratories and brought directly to Sample Receiving after they are collected. Sample receiving personnel should place these in cold storage as soon as possible.

   e. Samples collected locally by Empirical Laboratories personnel or local customers that hand deliver their samples. In some instances these samples may not have had time to cool down, however, these samples should have been placed on ice in an attempt to cool them to the proper temperature. It should be noted if samples are "Received On Ice" (ROI).

F. If several coolers are received at once, they must be inspected to determine the order in which the samples should be unpacked and logged in. The following priorities should be given:

   1. Any analyses, which have a 24-72 hour holding, time. A ***Short Holding Time Parameter List [Attachment V]*** is posted in the log-in room. It is the log-in person's responsibility to notify the analyst of such samples. In addition to notifying the analyst of samples with

short holding times, log-in personnel must log this information into a separate record book daily. It is the analysts' responsibility to review this information and initial each page at the end of each day.

2. Any sample which has almost exceeded its' holding time. (Especially watch for this with waters organic extractions, Solids and Sulfides, all of which have only 7 days). A list of parameters and holding times is posted in the log-in room.

   a. If a sample is received already out of holding time, the project manager must be contacted. The sample can be analyzed at the client's request, but it will be qualified on the final report as being analyzed out of holding time. The project manager must inform you of the client's need.

   b. If a sample is received with limited holding time remaining for any parameter it may be necessary to contact the project manager so that he/she can contact the client. If the sample has to be analyzed on a rush basis to meet the holding time a rush charge may apply. Also it may not be possible to analyze the sample within the holding time due to sample load, etc. A CAR must be completed.

3. Samples requiring rush turnaround.

   a. If sample(s) requires 24-hour turnaround they will take first priority. Other rush requests also have high priority.

   b. The Project Manager and/or Section Manager must be contacted for approval concerning any unscheduled rush requests.

G. Unpack all samples from the cooler. If there are any known or suspected hazards this must be done under a hood. All coolers from USACE projects should be unpacked under a hood. It may be necessary to rinse off the outside of the containers in the sink and/or wipe them off with a paper towel.

1. Visually inspect them for tampering and custody seals (if applicable). Sort and inventory the samples against the chain of custody by arranging them in the same order as they are listed on the chain of custody. Normally samples are assigned log numbers in the same order as they are listed on the chain of custody but for certain projects or situations it is acceptable to arrange them in a manner which will make them easiest to log in.

2. Check for leakage as this could compromise the sample integrity. If any spillage occurred in the cooler make sure this is noted. Also list all the other samples in the cooler as cross contamination could occur. A CAR must be completed and the Project Manager and/or the customer may need to be notified in these situations. It may be necessary to resample.

H. Check the chain of custody information against the information recorded on the containers. If these do not agree, contact appropriate person (s) - Project Manager, sampler, client, etc. All problems must be documented with a CAR.

1. If major changes are made on the chain of custody received from an engineering job, then the PE should submit written confirmation of these changes or make the corrections and initial them directly on the chain of custody.

2. Any error found on the chain of custody must be marked through with one line, initialed and dated and the correction written in.

I. Note any unusual requests, methodology, hazards (known or suspected) to the Project Manager and/or Laboratory Section Manager or analysts before the samples are actually logged in. Keep notes of any problems (improper containers, preservatives, temperature, or descriptions, etc.) A CAR must be completed but can be done so later in the day (see section IIIC), however, the analyst or manager may need to be notified immediately. If ever in doubt, fill one out!

II. Sample Log In

A. After samples have been unpacked, sorted and reviewed, they are then ready to be assigned log numbers and continue through the log in process. Make sure that the parameters for the samples are clearly marked on the chain of custody. Also refer to the "Incoming Project" file or routine client notebook in the log-in room to see if there is a work order or a memo to help you log in these samples. If we prepared the sample kits there should be a sample kit work order form. Contact the Project Manager if there are any questions, problems, etc.

B. Assign a work-order and sample number to each individual sample and record it on each sample container and the chain of custody.

1. All containers with the same description must have the same sample number even if they have different preservatives and require different tests. However, each different fraction (bottle type and/or preservative) should be designated with a letter (A, B, C, etc.)

2. Grab and composite samples from the same sample location must be considered as separate samples. It may be necessary to use "grab" or "composite" as part of the sample description to distinguish between the samples. Only assign different log numbers to them if the parameters are clearly marked as grab and as composite. Do not assume that VOC must be analyzed from grab samples so therefore the client must have taken a grab sample.

3. Sample numbers must begin with 001 at the beginning of each year (e.g. 0101001).

C. Check the following items and record this information on the chain of custody to further ensure sample integrity. A CAR must be completed if any of the following requirements are not met and it may be necessary to contact the client. We can perform the analyses in most cases and will do so with the client's approval, however the results may be qualified in some manner on the final report.

Preserving sample integrity throughout the log in procedure must be one of our section's top priorities. This includes not only ensuring that the proper chemical preservatives have been added but also that the samples are received and maintained at the proper temperature. ***When samples are unpacked they must be placed in cold storage as soon as possible even if they have not been through the entire log in procedure.*** All samples for NPDES compliance monitoring from North Carolina will be stored at a temperature range of 1.0 to 4.4°C. All other NPDES samples will be stored at 4.0 ± 2.0°C. On the days we receive a large volume of samples, or are short handed, etc., we may not be able to completely log in all samples until late in the day or even the next day. Samples should not set out at room temperature if there is a delay. The samples must temporarily be placed in cold storage until you are able to complete the log in procedure. This should also be done when we take lunch breaks.

[Make sure the VOC containers are not temporarily stored in a non designated VOC only storage area.]

1. Determine if the samples were received at the proper temperature. (See section IC)

2. The sample descriptions on the bottle should match those on the chain of custody. (See section 1H)

3. Check to determine if the proper chemical preservatives were added to adjust the sample to the correct pH. All regulatory compliance samples received from North Carolina that do not meet the preservation requirement will be segregated and the North Carolina State Laboratory will be notified of the non-compliance (919-733-3908). The samples will not be logged in or analyzed until written notification is received from the State of North Carolina to proceed with analyses. A list of parameters and the required chemical preservatives is posted in the log-in room. If Empirical Laboratories prepared and shipped out the sample containers they will have been pre-preserved unless instructed otherwise by the client. Complete traceability of the preservatives used to pre-preserve the sample containers and to preserve samples in the log-in area is required. A bound notebook must be used to trace this information and must include the following: Lot #, Type of preservative, Date Prepped, Amount and Analyst Name. This information must also be labeled on each container, re-pipetter, etc. that the preservative is stored in. Each lot of HNO3 used for Metals preservation must be tested prior to using them for preservation. These analyses are kept on file.

    a. The pH of each container (except VOA vials) which requires pH preservation must be checked. Do not open and check the pH of VOA vials in sample receiving/log-in.

This will be done by the VOC analysts at the time of analysis. In some instances it may be necessary to open the sample under a hood.

b. The pH of preserved samples are checked and confirmed using pH narrow range indicator paper. When the client request pH analysis on samples and they must be reported and measured for pH using the narrow range paper, rather then a pH meter, the accuracy of each batch of indicator paper must be calibrated to the nearest tenth versus certified pH buffer and recorded into a bound logbook in accordance with SW846 method 9041A pH Paper method.

c. When taking the pH reading, DO NOT PUT THE pH PAPER DIRECTLY INTO THE SAMPLE CONTAINER. Pour up a small aliquot and dispose of this volume after the pH is taken. For some samples (wastes) the indicator paper may not be accurate due to interferences. The observation of the appropriate color change is a strong indication that no interferences have occurred. If it appears as if there is interference, the pH must be measured using the pH meter. [See SOP ATSD-187 pH , Electrometric.]

4. The following guidelines must be followed to check pH preservation:

a. Water samples for Cyanide analyses must be preserved to a pH of >12 with NaOH upon collection. If the pH of these samples is between 11.0-12.0 upon receipt, and the samples are at the proper temperature and not over 48 hours old it will not be necessary to complete a CAR, however the sample should be adjusted to $\geq$12.0 unless project/client specific requirements are to contact the client first.

b. Water samples for Metals analyses must be preserved to a pH of $\leq$2.0 with HNO_3 upon collection. If the pH of these samples is between 2.0-.3.0 upon receipt, and the samples are not over 48 hours old it will not be necessary to complete a CAR, however the sample should be adjusted to $\leq$2.0. unless project/client specific requirements are to contact the client first.

c. Samples requiring analyses which are preserved with H_2SO_4 (i.e., Nitrogen compounds, Total Phenolics, Oil and Grease, Total Phosphorus, etc.) can be accepted up to a pH of 2.5 without a CAR, however the sample should be adjusted $\leq$2.0 unless project/client specific requirements are to contact the client first.

d. If a sample is not properly preserved, log-in personnel must either do the following:

- To meet project specific requirements, including all USACE projects, the client must be notified before preserving or adding additional preservative to the sample unless otherwise instructed. If the client instructs us to add chemical preservatives to a sample, complete traceability of the preservatives used is required (See section IIC, #3). A CAR must be completed.

- For other projects it may be acceptable to preserve the sample accordingly before the sample is placed in storage. Complete traceability of the preservatives used is required (See section IIC, #3). A CAR outlining the project and the steps taken must be completed.

e. In some instances it may not be possible to adjust the sample to the proper pH due to matrix problems which cause excessive foaming or require an unusually large amount of acid. Do not continue to add acid if a few mL's of acid does not lower the pH. Notify the Project Manager, Metals Manager and/or analyst. They will make the decision if the sample will be diluted, not analyzed, etc. A CAR must be completed in these situations. Make sure you note on the container and in the LIMS notes that the sample is not at the proper pH as well as any useful information (i.e., foaming, strong odor, etc.).

f. A CAR may not be required for samples generated in the Aquatic Toxicology Laboratories and brought directly to Sample Receiving after they are collected but before they are preserved. Log-in personnel must preserve the samples accordingly before they are placed in storage. Complete traceability of the preservatives used is required (See section IIC, #3). A CAR outlining the project and the steps taken must be completed.

5. Check to make sure samples are in proper containers and that there is adequate volume for all the parameters requested and no leakage.

6. If VOA vials are present, each vial must be inverted and checked for head space. "Pea-sized" bubbles (i.e. bubbles not exceeding 1/4 inch or 6 mm in diameter) are acceptable and should be noted, however a CAR is not required. This guidance is from SW846 Proposed Update II. Large bubbles or head space is not acceptable and a CAR must be completed. If this occurs, the client must be contacted. The samples can be analyzed with their approval, however the report will be qualified and the data may be questionable. All VOA vials will be preserved with $Na_2S_2O_3$ (0.2g) when chlorine is known to be, or suspected to be present.

7. All pesticide samples to be analyzed by method 608 will be checked by the sample receiving personnel for the correct pH range of 5.0 to 9.0. The pH of the sample(s) will be communicated via E-mail to the Section Manager and appropriate analyst.

8. All samples received for Cyanide must be checked for residual chlorine. The one liter sample container should initially contain 1 to 2g/L of Ascorbic Acid. All known chlorinated effluent samples will be checked for residual chlorine upon arrival at ELAB of Tennessee's Sample Receiving facility. Potassium Iodide starch indicator paper will be used for detecting the presence of residual chlorine. DO NOT PUT THE TEST PAPER DIRECTLY INTO THE SAMPLE CONTAINER. Pour up a small aliquot, neutralize, test and dispose of this volume after the sample is checked. If the test paper turns blue, the sample must be treated for residual chlorine. Add Ascorbic Acid, approximately 0.6g

at a time and recheck the sample until there is no residual chlorine present. If the sample required this treatment this information must be included in the LIMS notes. This must be done by log-in personnel before leaving the receiving area. It may be necessary to notify the Inorganic Manager and/or analyst.

9. Be aware of holding time requirements. (See section 1D)

D. Once sample containers have been numbered, they must be checked by another laboratory individual to ensure that the log number on the container matches the log number and sample ID on the Chain of Custody. A ***Sample Receiving Custody and Disposal Form [Attachment VII]*** must be completed each day. Samples should not leave the log-in area until this has been completed. *[see IIC; it may be necessary to temporarily store samples in cold storage until the samples can be second checked, the amount of time that the samples are at room temperature must be minimized as much as possible.]* A copy of this form should be given to the Project Manager at the end of the day. The original is to remain in Sample Receiving until the samples are disposed of. Once the document is complete, the original will be kept on file. The following information must be logged onto this form:

1. Client and Log #s
2. Date/Time Unpacked
3. Logged In/Numbered By (Initials)
4. 2nd Checked By (Initials)
5. Date/Time Placed in Cold Storage
6. Storage Area (Walk In, Hobart-VOCs, Quarantined Soils, Quarantined-VOC, Other)
7. Disposed of By/Date
8. Method of Disposal

E. Notify the proper analyst if samples have been logged in for analyses which have a 24-48 hour holding time or if a 1-2 day turnaround has been requested. The log number and description on sample (s) must be second checked before it is released to the analyst. (The analyst can second check the sample, but must initial the custody form.)

III. Sample Storage

A. After samples have been correctly logged in they are then transferred to one of the following cold storage areas and arranged in numerical order by the assigned log in/LIMS sample number. ***Note that aqueous VOC samples must be segregated from all other samples.***

1. Hobart Refrigerator in Sample Storage Room: All aqueous VOC's must be stored in this refrigerator. Storage blanks consisting of organic free water from the laboratory may be required for specific projects. These will be analyzed for VOCs only.

2. Walk In Refrigerator in Sample Storage Room: All aqueous samples for all analyses must be stored in this refrigerator

3. Soil Walk-In Refrigerator in back BC Laboratory: All quarantined and non-quarantined soil samples for all analyses must be stored in this refrigerator.

B. Quarantined soils are those quarantined by the US Department of Agriculture. These soil samples must be segregated from other soil samples during storage. A separate disposal log must be maintained for these soils including the location, date and quantity of the soil received and processed. Soil residues and from quarantined samples must be treated according to regulations after testing (see Sample Disposal SOP). Quarantined soils are defined as:

1. Soil taken from much of the southeastern US and parts of New York and Maryland at a depth of three feet or less. *Soils from three feet or more are not regulated provided they are stored separately.* A map of the regulated areas in the United States entitled ***Soil Movement Regulations [Attachment VIII]*** is posted in the log-in room.

2. All soils taken from foreign sources, US. territories and Hawaii .

NOTE: All soils are treated as quarantined soils and are disposed of in accordance with USDA regulations. Above for information purposes only.

C. All samples must be stored in one of the three refrigerators detailed above with the following exceptions:

1. Matrices that may be adversely affected by the cold temperature. (e.g. surfactant samples, multi-phase samples)

2. Highly contaminated waste or product type samples that could jeopardize the integrity of other samples in the walk in cooler. Often these can be stored at room temperature. If these require refrigeration see the Project Manager for other options.

D. The temperature of each sample refrigerator must be monitored and recorded each day by Wet Chem personnel by the following method. A Mercury thermometer or digital min/max thermometer with 1° increments must be used. Each thermometer must be calibrated against a NIST certified thermometer once a year(**digital thermometers quarterly**) and this information recorded in a bound notebook. The Certificate of Calibration for the NIST thermometer is kept on file at the QAO's desk. The thermometers must be tagged with a unique identification, the date calibrated and the correction factor.

The tolerance range for all refrigerators is 1 to 6°C. This range and the range using the corrected reading must be posted on the outside of each cooler. If the temperature exceeds this range, corrective action measures must be put in place immediately. A CAR must be completed specifically noting the date and time the problem was discovered. The Project Manager, Laboratory Director and Technical Director will be notified in order to assess the situation. It may be necessary to put a service call in to the refrigeration repair service.

E. All personnel removing samples from any refrigerator must sign them in and out. This is done by completing the ***Sample Custody Form [Attachment IX]*** which is attached to the door of each refrigerator. These completed forms are kept on file [see section III, #4F]

F. The water walk in refrigerator in the sample room is the largest refrigerator and stores a large majority of the samples. A back up compressor is hooked into the system and scheduled to automatically come on if the main compressor fails. There is a digital min/max thermometer, which monitors the temperature 7 days a week. This thermometer will be calibrated quarterly against the NIST thermometer.

G. As stated above the temperatures for all refrigerators that samples are stored are checked each day Monday-Friday and monitored seven days a week with min/max thermometers. Pay close attention to these readings and watch for signs of possible problems.

H. A maintenance record book is kept for each refrigerator.

I. Samples must be held for a minimum of 30 days after the final report unless specified otherwise. For USACE projects, samples must be held for a minimum of 60 days after the final report unless otherwise specified. See SOP ATSD 405 entitled Analytical Laboratory Waste Disposal SOP for guidance on disposal of samples.

IV. Laboratory Information Management System (LIMS)

A. Log the sample information into the LIMS for each sample. Every attempt should be made to get every sample logged into the LIMS by the end of the day. All information should be clearly stated. Note: the work-order number (w.o.#) can be assigned prior to entering all sample information. Make sure the w.o.# number is recorded on the chain of custody to help. After opening the main menu of the LIMS click on WORKORDERS and then click on ADD to create a new workorder. You will see the following:

1. ***Client I.D.:***

   Select the client I.D. by clicking on the pull-down and choosing from the client list. This list is not always in alphabetical order. If the desired client is not on the list, a new client must be created (See OMEGA LIMS handbook).

2. ***Project I.D.:***

   Click on project and choose the project I.D. The projects will be client specific. After the project is chosen the "project information" area should fill in. The "project name", "QC level", "TAT", and "Report to" information should also appear. If there are no project choices, a project must be created (See OMEGA LIMS handbook). There are two types of projects:

   a. Internal—Empirical Laboratories projects; use job/task #

   b. External--direct laboratory clients; use X------- where the last two spaces are a counter. Example: XMONWW01

      [Pay close attention as a few clients are actually both.]

3. ***Comments:***

   Record any additional comments or observations. This includes but is not limited to information concerning rush turnaround, deliverables or other QC requirements, analyte concentrations, safety issues, quarantined soils, CAR #s, preservation or matrix problems, etc.

4. ***Rec. by:***

   Enter the initials of the person who received the samples.

5. ***Received:***

   Enter the date and time received separated by a space and using military time. Example: 1/1/02 16:30

6. ***Date Due:***

   After the date and time received have been entered, tab down to date due and this date will be calculated.

7. ***Coolers:***

   Click on "Coolers" tab and enter temperature on receipt.

8. ***Invoice Info:***

   a. Click on the Invoice Info. tab and enter any discount or surcharge

b. Add the purchase order number when applicable. A listing of yearly/blanket PO #'s is posted in the log in room. This is periodically updated by the Project Manager.

After these items have been completed, click on the Login button to continue.

9. ***Client Sample I.D.:***

a. Only abbreviate if description is too long for the spaces allotted in the LIMS or on the computer tracking logs. This information should come directly from the chain of custody. The sample ID entered into the LIMS will be the sample ID on the final report.

b. Include date as part of the description if this is the only way to differentiate the samples. This should always be done with certain clients who have requested it and may be necessary for samples received from the wastewater treatability laboratory.

c. When logging in trip blanks for VOA list them as "Trip Blank # _____". This information should be on the containers. A log book must be kept in the sample kit room which lists all trip blanks and the date they were filled. This will ensure consistency with the descriptions for trip blanks. Make sure you record the trip blank on the chain of custody if it is not listed.

10. ***Collection Date:***

Enter the date and time the sample was collected. You must use military time and separate by a space. Often the time collected is not given. Although this is a sampling requirement, this information may not be crucial unless a parameter with a short holding time or a data deliverables package is required. All attempts should be made to get all our clients to supply this information.

11. ***Matrix:***

Click on pull down and select matrix. Many times it is difficult to select the matrix and log-in personnel must use their best judgment. Keep in mind that the detection limits and units on the LIMS reports are linked to the matrix. In some cases it may be necessary to ask the Section Managers about the matrix selection.

12. ***Bottle Type:***

Click on the pull down and select the appropriate bottle type.

13. ***# Containers:***

Enter # of containers of the same bottle type.

14. ***COC ID:***

Enter this number for USACE and other specified projects.

15. ***Comments:***

Enter any information that is applicable at the sample level.

16. ***Field Data:***

Click on field data tab and enter field information.

Sampler: Enter in the sampler's initials. If this information is not available leave this section blank or record NG for not given. This information should be given, however it may not be crucial. All attempts should be made to get all our clients to supply this information.

a. pH: Enter the field pH

b. Site Type: Enter F for "field" pH
c. Enter R for "lab" pH

d. **Technique**: Enter sample type (grab or composite)

17. ***Tests:***

a. Click on the box below Tests and then click on the pull-down. Select parameters from this list.

b. Pay close attention when selecting the analyses, as more than one method may be listed in the LIMS directory for each type of analyses. A few examples of these are: TPH, VOA, Ammonia, Oil and Grease, Phenol and Metals. Do not guess at the method. If the method is not known, take the time to ask before selecting it in the LIMS. If only specific organic analytes are requested this information must be forwarded to the Organic Manager.

c. For NPDES samples note the following requirements: A list of ***Routine NPDES clients [Attachment XI]*** is posted in the Sample Receiving Room. This is only a guide and should not be considered absolute. Always ask if you are ever in doubt. Remember that some clients may send in samples for NPDES monitoring and RCRA monitoring, etc.

1. Samples that require Ammonia analysis must be logged in and analyzed by the distillation method. This is per 40 CFR 136 that states that "Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary." If we choose to do this for any client, this information must be documented and kept on file. It is the responsibility of the Inorganic Manager to track this information and inform the sample receiving group of any clients that may fall into this group.

2. All NPDES samples that require organic analyses must be logged in for 600 series methods (608 for Pest/PCB, 601/602 or 624 for VOA and 625 for BNA). Samples from RCRA projects that require organic analyses must be logged in for SW-846 methods (8081/8082 for Pest/PCB, 8260 for VOA and 8270 for BNA.)

   a. Non aqueous samples for organic analyses must list an extraction method; low vs. medium and sonication vs. soxhlet.

   b. For most non-aqueous samples, it will be necessary to log the sample in for % solids in order for the sample result to be reported on a dry weight basis. The general rule of thumb is that all soil and sediment samples will be reported on a dry weight basis unless otherwise requested from the client. Separate LIMS codes are set up for the Metals analyses (soil vs. soil dry weight.)

   c. It may be necessary to add in additional non testing codes such as sample kits, labor hours, mileage, ISCO rental, QC requirements, etc. for billing purposes. You can add these while adding analytical tests.

If bottles are received that are the same sample volume but have different preservatives but you must "add fractions".

18. ***Add Fraction:***

To add a fraction click on the "Add Fraction" button. The cursor will take you back to step 12. From here you may proceed to enter additional sample containers and associated parameters.

19. ***Add Sample:***

Click on the "Add Sample" button to add a sample within the same workorder. The cursor will return to step nine where you may enter the next sample.

Once all the tests have been selected and all samples have been added in the workorder, login of this group of samples is complete.

V. Daily Follow Up for Sample Receiving/Log In

A. Wipe out the inside of coolers and return all Empirical Laboratories coolers to the sample kit room. Discard any coolers that are cracked, broken or filthy.

B. Complete the short holding times log book as required. This must be done as early in the day as possible.

C. If any samples were received for RUSH turnaround, then a ***RUSH SHEET [Attachment XII]*** must be completed and distributed to all laboratory personnel via e-mail. These are copied on yellow paper in order to call attention to their importance. If ever in doubt of which analysts should be notified, pass them out to everyone. Always give copies to the Laboratory Director, Administrative Assistant and Section Managers. It may be necessary to send out two RUSH sheets per day (one around mid-day and the other at the end of the day).

D. Analyze for pH and corrositivity as requested. (See SOP for pH)

E. Complete any required CARs.

F. At the end of the day organize all paperwork received and generated for the day . The following should be given to the Project Manager (section supervisor):

1. The original chain of custodies and yellow original or copy of each.

2. Any information (letters, regulatory limits, etc.) from a client which was received with any samples.

3. All CARs.

4. LIMS sample receiving logs.

5. Copies of any RUSH sheets which have been distributed

6. Sample Receiving Custody and Disposal Form.

7. Cooler receipt form if required.

G. All the above information from the day will be reviewed as soon as possible.

1. All LIMS logs must be 2nd checked by a different person than the person entering the information into the LIMS. Each set of logs must be initialed dated by the person 2nd checking. These will be kept on file at the Project Manager desk.

2. If any corrections or changes are required, all laboratory personnel will be notified by distributing a ***Sample Log Change Form [Attachment XIII]*** These are copied on green paper in order to call attention to their importance and are routinely referred to as "green sheets". A green sheet will also be sent out if a client adds or deletes any parameters, changes sample IDs, etc.

H. The Testing Coordinator will distribute the following (on a daily basis if possible) after they have been through the 2nd QA check:

1. Copies of the LIMS receiving reports to necessary laboratory personnel.

2. Original (white copy) chain of custodies are given to the Project Manager. These will be sent with the final report to the client.

3. Finalized/approved CARs must be sent to the:

   a. Organic Manager

   b. Inorganic Manager

   c. Laboratory Manager

   d. Laboratory Director {optional}

   e. Quality Assurance Officer

   f. Administrative Assistant

   g. Client {optional}

4. Copies of any project/sample specific information to the Section Manager and analysts.

I. Information will be filed as follows:

1. Chain of custodies:

   a. Original (white copy) are returned to the customer with the final report.

   b. Yellow copy originals or photo copies will be filed by client and kept in the Sample Receiving Room.

c. Photo copies will be kept in a notebook in numerical order in the Sample Receiving Room.

d. Pink copies should be retained by the sampler.

2. CARs

a. Stapled to the yellow copy original chain of custody kept by Sample Custodian

b. Stapled to photo copy of chain of custody in log-in room

c. CARs can be found at K:\log-in\logcar(year, ie 04).

3. Green Sheets and RUSH Sheets

a. Copy at Project Manager's desk.

b. Copy in log-in room.

4. At the end of each year, files for that year are boxed and archived. Make sure files are labeled properly and place them in banker's boxes. Complete a storage box file form with as much detailed information as possible. The Laboratory Administrative Assistant will label and number the boxes and incorporate the storage boxes into the laboratory file archive system. Boxes containing files from Sample Receiving are kept on site for 1-2 years and then may be moved to off site storage upon release from the Project Manager.

VI. Miscellaneous

A. All projects which require deliverables or other QC requirements should be listed in the notes section of the LIMS.

B. If samples are received from a new client or a new job number that is not in the LIMS, a new client code must be set up. This information should be on the chain of custody or it may be necessary to contact the customer if the information is incomplete.

C. All sediments received must be examined to see if there is a water layer. If there is a water layer it must be decanted. It is the log-in person's responsibility to do this except for VOA samples. This will be done by the VOA analyst. If water is decanted this must be noted in the comments section of the LIMS.

D. Samples from the Aquatic Toxicity Laboratory (ATL) are logged into the LIMS for billing and long-term tracking purposes. The receiving information and proper assignment of test's are reviewed by the ATL Manager. The samples are then logged in by ATL personnel.

E. A flow chart outlining sample receiving and the flow of data, reporting and invoicing is attached as ***Attachment XIV.***

F. A ***Telephone Conversation Log [Attachment XV]*** may be required to document information and may be attached to or used as a CAR.

G. All log books used in the Sample Receiving and Sample Storage Areas are numbered. The following log books are presently maintained. All log books must be "Z"ed out. The Testing Coordinator will review the log books each week to check for completeness.

Log Book ID	**Log Book Description**
SRLB #3	pH Paper Calibration,pH Meter Calibration and Maintenance
SRLB #4	Tracking of VOC Trip Blanks, Organic Free Water and Chemical Preservation

Attachments to SOP 404

II	Chain of Custody Record
III	Corrective Action Report for Sample Receiving/Log In
IV	Cooler Receipt Form (used for USACE project)
V	List of Short Holding Time (Immediate-72 hrs.) Parameters
VII	Sample Receiving Custody and Disposal Form
VIII	Map of Quarantined Soil Areas in the US.
IX	Laboratory Sample Custody Form for Walk In Refrigerator
X	Container Codes for the LIMS
XI	Routine NPDES Clients
XII	RUSH Sheet
XIII	Sample Log Change Form (Green Sheet)
XIV	Flow Chart, Laboratory Sample Tracking System
XV	Telephone Conversation Log

[Attachments I and VI were removed during the editing process and not added to the SOP.]

STANDARD OPERATING PROCEDURE (SOP) FOR LABORATORY SAMPLE STORAGE, SECURE AREAS AND SAMPLE CUSTODY

SOP NUMBER: SOP-410

REVISION NUMBER: 4

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 02/10/06

DATE OF LAST REVIEW: 02/10/06

STANDARD OPERATING PROCEDURE (SOP) FOR LABORATORY SAMPLE STORAGE, SECURE AREAS AND SAMPLE CUSTODY

Empirical Laboratories, LLC is located on the fifth floor of a building which is locked and monitored by a guard after normal business hours. No unauthorized personnel are permitted within the facility without a proper escort and a visitor's badge. During non business hours, all doors to the building are locked and the elevators are security coded (i.e. a code must be entered in order to get the elevator to open on the fifth floor.) All stairway doors are locked and only Empirical Laboratories, LLC personnel have a key to the fifth floor stairway door. The doors to the lab in the hallway have a key code. There is a buzzer at the door to Login to allow entry for sample and supply deliveries.

The majority of samples are shipped in coolers by couriers such as Federal Express and UPS. All couriers are generally received in the Shipping/Sample Receiving (SR) area on the fifth floor. The laboratory is located close to Federal Express (FedEx) distribution station, therefore we pick up our coolers at the FedEx location on Saturdays and transport them directly to the laboratory. Some coolers and/or samples are delivered directly to the SR area by the sampler and/or client. The SR personnel must not leave any packages/cooler without authorized receipt from laboratory personnel. Samples must be accompanied by some type of chain of custody record. Sample receiving personnel sign, and list the date and time received on the chain of custody. The time received must reflect the actual time or validation date and time of receipt for the samples although they may be placed in cold storage and logged into the system at a later time. The method of delivery is listed on the chain of custody. A copy of the airbill (if available) is attached to the chain of custody.

Once sample containers have been assigned a laboratory ID number, they must be checked by another laboratory individual to ensure that the log number on the container matches the log number and sample ID on the Chain of Custody. A Sample Receiving Custody and Disposal Form (attached) must be completed each day. Samples should not leave the log-in area until this has been completed. A copy of this form must be given to the Testing Coordinator at the end of the day. The original

is to remain in Sample Receiving until the samples are disposed. Once the document is complete, the original will be kept on file. The following information must be logged onto this form:

- Client and Log #s
- Date/Time Unpacked
- Logged In/Numbered By (Initials)
- 2nd Checked By (Initials)
- Date/Time Placed in Cold Storage
- Storage Area (Walk In, Hobart-VOCs, Quarantined Soils, Quarantined-VOC, Other)
- Disposed of By/Date
- Method of Disposal

Original samples are stored in following areas of the fifth floor. The Water Sample Storage and Sample Receiving rooms are locked during non business hours. Only laboratory personnel have keys to these areas.

1. Hobart Refrigerator in Sample Storage Room: All water VOCs must be stored in the refrigerator.

2. Walk In Refrigerator in Sample Storage Room: All waters for all analyses except VOCs must be stored in this refrigerator.

4. Soil Walkin Refrigerator for all soils.

All soils are treated as quarantined.

All samples must be stored in one of the three refrigerators detailed above with the following exceptions:

1. Matrices that may be adversely affected by the cold temperature. (e.g. surfactant samples, multi-phase samples)

2. Highly contaminated waste or product type samples which could jeopardize the integrity of other samples in the walk in cooler. Often these can be stored

at room temperature. If these require refrigeration see the Testing Coordinator for other options.

Any person removing samples from the storage areas listed above, must sign them out on a laboratory custody sheet (attached). The individual performing the processing becomes responsible for the samples at this point. The samples are maintained in the secure possession of the individual processing the samples. When the processing is completed, the samples are returned and signed back into the appropriate storage area. It must be noted if the entire sample volume was used and that the container was discarded.

Sample extracts and digestates are stored in the following areas:

1. All metals digestates are stored in the metals instrument laboratory. The transfer from the digestion analysts to the ICAP analysts is documented in the metals digestion log book.

2. Non ZHE TCLP extracts are returned to the refrigerator in which the original samples are stored. For ZHE samples, the extract is returned to the refrigerator in which the original VOC sample containers are stored.

3. Extracts from medium level VOC analyses are also stored in the VOC sample refrigerator.

4. All Organic extracts for are stored in a "Hobart" side by side refrigerator in the organic extraction laboratory.

The generation of all sample extracts/digests and their movement through the laboratory will also be tracked on a laboratory custody sheet or in a log book. The individual performing the processing becomes responsible for the samples at this point. The samples are maintained in the secure possession of the individual processing the samples. When the processing is completed, the extracts are returned and signed back into the appropriate storage area. The metals digestates are not removed from the metals instrument laboratory.

After the analytical results have been reported, the original samples, sample extracts, and digestates will remain in secure storage until they are disposed of in accordance with the Waste Disposal Standard Operating Procedure. Samples will be held for a

minimum of 30 days after the final report unless specified otherwise. Sample extracts and digestates are held for a minimum of 60 days after the final report unless project specific requirements state otherwise. See SOP No. 405 entitled Laboratory Waste Disposal SOP for guidance on disposal of samples.

The following personnel as of February 10, 2006 have access to all sample storage areas:

Teneshia Acklin	Herbie Johnson
Amy Barnett	Andrew Kim
Andy Barton	Jessica Lawrence
Latrice Bragg	Marcia McGinnity
Susan Burchfield	Tim McCollum
Roger Burr	AntonioMontiero
Rick Davis	Brian Richard
Barbara Dawson	Andy Robinson
Betty DeVille	Kara Seward
Wanda Frye	Anne Talbot
Gary Forsythe	Ted Taylor
Sonya Gordon	Binta Tolbert
Mary Halter	Randy Ward
Jade Holliman	Renee Vogel

In the event that an employee is terminated, the supervisor is responsible for collecting the employee's keys.

For additional information see SOP No. 404 entitled Laboratory Sample Receiving, Log-In and Storage.

THE LABORATORY SAMPLE CUSTODIAN'S DUTIES AND RESPONSIBILIITES

SOP NUMBER: SOP-415

REVISION NUMBER: 3

APPROVED BY:

SECTION MANAGER

TECHNICAL DIRECTOR

EFFECTIVE DATE: 02/13/06

DATE OF LAST REVIEW: 02/13/06

THE LABORATORY SAMPLE CUSTODIAN'S DUTIES AND RESPONSIBILITES

The Sample Custodian is responsible for the receiving, log in, tracking and disposal of all samples. The duties of this position are performed by the persons in the sample receiving section of the laboratory. These individuals are the primary custodian, secondary custodian and section supervisor. Although other laboratory personnel may assist with the duties, this is done under supervision and direction of one of the three individuals listed above.

The sample custodians are responsible for the following:

- Receive all samples for the analytical laboratory and maintain chain of custody. This includes documenting the validated time/date of receipt.

- Maintain the flow of samples through the log in process and make them available to the analysts on a timely manner. This includes prioritizing samples/projects based on turnaround requests and holding times.

- Assign the correct laboratory ID sample numbers and validate that this information is properly labeled on the containers and entered into the Laboratory Information Management System (LIMS).

- Validate that every sample proceed through all steps of the log in process. This includes checking the following to determine that the sample integrity has been upheld from the time the sample is collected until it is received in the laboratory: proper containers with ample sample volume, correct preservation, sample dates/times to ensure that holding times can be met, condition of the sample containers, headspace of vials for VOC analysis, sample ID discrepancies and completeness of the chain of custody.

- Communicate any information or specific requests by the client that are listed on the chain of custody, i.e., method information, detection limits, specific analytes, reporting information, turnaround information, potential hazards etc. They are also responsible for

forwarding any additional information that may be received along with the samples, i.e. permit or regulatory information, letters, etc. to the laboratory managers.

- The sample custodian is personally responsible for continuing to uphold the sample integrity throughout the log in procedure and until the time when the samples are properly stored and disposed.

- Ensure that samples are transferred into the proper storage area and that these secure areas are locked after hours.

- Maintain all log books used in the section. These must be kept up to date, complete, neat and orderly.

- The Wet Chemistry Section designates a person that monitors the temperatures of all cold sample storage areas and records them daily. Corrective action measures are implemented when necessary. Temperatures must be maintained in the range of 1 to 6°C. Cold storage temperatures must not exceed 4.4°C for all North Carolina compliance samples.

- Maintain the sample receiving and sample disposal areas in a clean, orderly and safe manner.

- Follow good laboratory practices and safety procedures.

- Communicate all problems, discrepancies, etc. to the section supervisor and documenting them by completion of a Correction Action Report (CAR) when necessary on a timely basis. (Example attached)

- In situations where the client cannot be contacted, the sample custodian along with the section supervisor must apply the best judgment on how to handle he samples or situation.

- Complete all the necessary paperwork and section forms including RUSH Forms, Short Holding Times (48 hrs. or less) Log Book, Sample Receiving Correction Forms, Cooler Receipt Forms, LIMS daily print outs, Sample Receiving Custody and Disposal Form, etc. in a timely manner. (Examples of forms are attached).

- Dispose of all samples in a manner that is safe, cost efficient, timely, meets project requirements and is in accordance with hazardous waste regulations.

- The sample custodian(s) are responsible for compliance of all procedures outlined in this SOP and the following SOPs. They must maintain personal copies of each SOP.

404	Laboratory Sample Receiving, Log In and Storage
405	Analytical Laboratory Waste Disposal
406	Subcontracting Samples
407	Sample Kit Preparation
409	pH; Paper Method
187	pH; Electrometric

Appendix D

APPENDIX D
Response to Comments

SUBJECT: Response to review comments for the Draft Quality Assurance Project Plan, Remedial Investigation, Part 1, at Acid Area 1, Former Plum Brook Ordnance Works (PBOW), Sandusky, OH, February 2007, Prepared by Jacobs Engineering Group, Inc., Contract Number DACW62-03-D-0004-0007

Reviewer: Carol Lee Dona, USACE - CX , Process Engineering

Comment # 1, Table 3-1: Please include the field water quality paramters (dissolved oxygen, oxidation reduction potential, temperature, specific conductivity, turbidity, and pH). Also please include the instrumentation that will be used to collect the field parameters.

Response: These parameters are presented on Page 2 of the table. These parameters will be analyzed at the laboratory per the specified method.

Reviewer: Chung-Rei Mao, USACE - CX Chemistry

Comment # 1: Page 1-1, Section 1.0: DoD "Quality Systems Manual for Environmental Laboratories," Version 3, January 2006 should be referenced and used for data quality control purpose. It replaces Appendix I of EM 200-1-3.

Response: The DoD QSM will be referenced instead of Appendix I.

Comment # 2: Page 2-1, Section 2.1: Please justify why a third-party data validation is not required for this investigation, and also clarify the statement of "data set will be validated following NFG logic and qualification flags."

Response: Third party validation has historically not been required at this site. A QA data assessment will be performed comparing the results from the primary and QA labs, as indicated in the QAPP.

The statement referencing NFG logic will be replaced with the following statement "...this data set will be validated following validation protocol set forth in the QSM..."

Comment # 3: Page 3-1, Sections 3.1.1 ~ 3.1.4 & Tables 3-1 & 3-2: Suggest that the most recently published SW-846 methods (i.e., 8260C, 8270D, 8330B, etc.)

Response: The decision to use older, but substantively the same, SW-846 methods (8260B, 8270C, 8330A, etc.) was based on both historical methods used at the site and the fact that the laboratories have not switched to the newer methods. Data quality objectives will not be affected by using the older SW-846 methods.

Comment # 4: Page 3-2, Sections 3.1.3 & Page 3-3, Section 3.1.4: Please verify and explain why preparation Method 3520C is required for aqueous SVOC and PCB samples and Method 3510C is required for TCLP SVOC samples. It is not clear which preparation methods, Method 3510C or 3520C, will be used by the primary and QA labs, because Appendix C does not contain any ELAB's SOPs for aqueous sample preparation and contains STL-Chicago's Method 3510C SOP only. Suggest that the same preparation method be used by both the primary and QA labs to minimize data variances, which might be caused by different preparation methods. In addition, if STL-Chicago uses Method 3520C, please ensure that the lab will not use a so called "One-Step Extraction and Concentration apparatus" that has shown

low and inconsistent analyte recoveries, compared with regular extractor and concentrator. STL-Chicago agreed on not using it for Corps projects.

Response: Extraction Method 3510C will be used throughout. Method 3520C will not be used. The text and Tables 3-1 and 3-2 will be corrected to reflect this.

Comment # 5: Page 3-3, Sections 3.2.1: As a rule of thumb, the MRLs should not be greater than one-half of the action levels, assuming data uncertainty RSD ≈ 10% and tolerable decision errors $\alpha = \beta = 0.05$. Suggest that the MRLs for all project-specific target analytes be set at no greater than one-half of Region IX PRGs for more reliable decision making.

Response: MRLs are set by the laboratories based on their lowest concentration calibration standard, and thus may occasionally be greater than one-half of the Region IX PRGs. As noted in the in the text, some MRLs and MDLs can't meet the risk-based goals because these goals were developed based solely on risked-based calculations, regardless of existing methodology. When possible, the MRL is set at a concentration no greater than one-half the PRG value.

Comment # 6: Table 3-3: The MRLs of certain target analytes (e.g., vinyl chloride, TCE, 1,2,4-trichlorobenzene, and mercury of the QA lab and all Aroclors of the primary lab) are set too low versus the MDLs so that data reported near the MRLs would have excessive data uncertainty. MRLs should be established at a factor of five to ten times the MDL for the majority of target analytes, but no lower than three times the MDL for any target analyte. In addition, analytes with PRGs greater than the MRLs were not shaded as discussed in Section 3.2.1.

Response: As stated above in the response to Comment #5, the MRLs are the lowest concentration calibration standard; the MDLs are determined using 40 CFR Pt 136, Appendix B, with the laboratory running the lowest calibration standard. For the compounds mentioned above, the laboratories will be asked to reassess their MDLs, and data reported as detects near the MRL will be assessed on a case-by-case basis during data validation.

Analytes with PRGs greater than the MRL have been shaded, and the updated tables are included as an attachment to the RCL.

SUBJECT: Response to review comments for the Draft Quality Assurance Project Plan, Remedial Investigation, Part 1, at Acid Area 1, Former Plum Brook Ordnance Works (PBOW), Sandusky, OH, February 2007, Prepared by Jacobs Engineering Group, Inc., Contract Number DACW62-03-D-0004-0007

Reviewer: Julie Weatherington-Rice, TAPP

1. **Jacobs has done a nice job of summarizing the information in this report in their series of tables.**

Response: Comment noted.

Table 3-1 Plumbrook Ordnance Acid Area 1 Sample Summary

2. **This table is missing notes at the end of the table that defines what the number (1) at the end of "Trip Blank" means and also what the abbreviation "MS/MSD" stands for.**

Response: the notation was removed from "Trip Blank" and "MS/MSD" was added to the acronym list.

Tables 3-11 Target Compound Lists

3. **There is an (*) notation with the Region 9 PRG limit. However, there is no note at the bottom of this table to explain what the (*) means.**

Response: A footnote has been added.