FINAL SITE-SPECIFIC FIELD SAMPLING PLAN

REMEDIAL INVESTIGATION, PART 1, AT RESERVOIR NO. 2 BURNING GROUND (2BG)

FORMER PLUM BROOK ORDNANCE WORKS SANDUSKY, OHIO

Prepared for:

DEPARTMENT OF THE ARMY
NASHVILLE DISTRICT, CORPS OF ENGINEERS
NASHVILLE, TENNESSEE
CONTRACT DACW62-03-D-0004-0002

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COMPLETION OF INDEPENDENT TECHNICAL REVIEW

Jacobs Engineering Group, Inc. has completed the **Final Site-Specific Field Sampling Plan** for the **Reservoir No. 2 Burning Ground 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.

Mike Hanchey by MW	Chemist	5/5/04
(Signature)	(Discipline)	(Date)

Independent Technical Review Team Leader and Team Members

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Al Hardesty	Hydrogeologist	May 5, 2004
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JE Site-Specific FSP Author

CERTIFICATION OF INDEPENDENT TECHNICAL REVIEW

Significant concerns and the explanation of the resolution are as follows (Describe the major technical concerns, possible impact, and resolution):

Comment: All comments on draft require review.
Resolution: Response to Comments (RTC) are included as Appendix A. All modifications, as per RTC, are incorporated.

Comment:

Comment:

Comment:

Comment:

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

Virgil W Janssen (Signature) 5/5/04 (Date)

(Project Manager)

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LIST OF ACRONYMS AND ABBREVIATIONS

amsl	above mean sea level
AOC	area of known contamination
ASTM	American Society for Testing and Materials
2BG	Reservoir Number 2 Burning Ground
bgs	below ground surface
°C	degrees Celsius
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
PCB	polychlorinated biphenyls
PID	photoionization detector
QAPP	Quality Assurance Project Plan
QCP	Quality Control Plan
RBC	risk based criteria
RI	remedial investigation
SAIC	Science Application International Corporation
SI	site investigation
SSFSP	Site-Specific Field Sampling Plan
SHP	Site Wide Safety and Health Plan
SSHP	Site-Specific Safety and Health 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 studies of the environmental impact of suspected hazardous waste sites 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 Group (Jacobs) is contracted to conduct Part 1 of a Remedial Investigation (RI) of the Reservoir No. 2 Burning Ground (2BG). Figure 1-1 shows the location of the 2BG.

As an attachment to the PBOW Sitewide Sampling and Analysis Plan (SWSAP) (Jacobs 2004), this Site-Specific Field Sampling Plan (SSFSP) has been prepared for the work to be conducted in support of the 2BG RI, Part 1 at PBOW. This SSFSP will be used in conjunction with the SWSAP (Jacobs 2004) 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 (SSQAPP) has been prepared as part of this Site-Specific SAP. A Site-Specific Safety and Health Plan (SSHP) has also been prepared separately for this RI that will be used in conjunction with the Sitewide Safety and Health Plan (SHP)(Jacobs 2004b).

1.1 SITE HISTORY AND CONTAMINANTS

A preliminary assessment (PA) conducted by Science Application International Corporation (SAIC) at PBOW (SAIC, 1991) identified the presence of a burn ground west of Reservoir No. 2, but the location was approximate and the dimensions were unknown. The Dames & Moore records review (Dames & Moore 1995) states that SAIC's project files included a 1963 letter written to the demolition and decontamination subcontractor, Ravenna Arsenal, describing proposed work at the site. Ravenna Arsenal was directed to "clear the trinitrotoluene (TNT) burning ground near Reservoir No. 2 of all debris, decontaminate ground, and restore ground to proper grade." During the records review, Dames & Moore representatives spoke with a former PBOW employee, who reported a burning ground located south of Reservoir No. 2, in an area formerly used by Plum Brook Station (PBS) as a ball field (Dames & Moore, 1995).

A subsequent review of aerial photographs taken in 1950, 1958, and 1968 of the identified area indicated the presence of a disturbed area with a rectangular berm (1950), a pronounced burn ground (1958), and a large cleared area (1968), attributed to the clearing of a fire break around the burn ground (Figure 1-1). Dames & Moore estimated the size of the burn ground as 125 ft. wide by 175 ft. long, based on the 1950 aerial photographs.

The record review indicated that 2BG is located south of Reservoir No. 2, and may have been previously referred to as the "Fox Road Burning Area." The site is estimated to have been used from at least 1950 through 1962 (Dames & Moore 1995).

A Site Investigation (SI) of 2BG was conducted in 1996 by IT Corporation (IT) to delineate the boundary of the burn area, to determine the existence and nature of contamination, and to evaluate potential risks to human health and the environment (Figure 1-1). Geophysical surveys were conducted to identify subsurface anomalies. Based on these surveys, four exploratory trenches were excavated within the boundary of the burn area. Eight soil borings were completed to a depth of seven feet to characterize lithology and to collect soil samples for off-site laboratory analysis. 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 and subsurface soil exceeding the RBCs include the following:

- Polynuclear aromatic hydrocarbons (PAHs): Benzo(a)pyrene
- Nitroaromatics: 2,4-Dinitrotoluene, 2,6-Dinitrotoluene 1,3,5-Trinitrobenzene, 2,4,6-Trinitrotoluene, 4-Amino-2,6-Dinitrotoluene
- Polychlorinated biphenyls (PCBs): Aroclor 1260

Inorganic contaminants in surface and subsurface soil exceeding both the RBCs and the established background values are limited to lead, aluminum, and thallium.

1.2 SUMMARY OF EXISTING SITE CHARACTERISTICS

The 2BG site is located approximately 400 feet (ft.) south of Reservoir No. 2 at the former PBS ball field between Ransom Road and Campbell Street, based on 1950 aerial photography that delineates a cleared area approximately 260 ft. long and 150 ft. wide. Low-altitude, oblique-angle photos indicate that the burning ground site occupied the central portion of this cleared area. Re-grading of the area in 1963 removed all visible evidence of the former burn area, as observed on the 1968 aerial photographs.

1.2.1 Physical Setting

The 2BG site physical features include a former burning ground located in an open field and a drainage ditch at the northern edge of the field. The ground surface is relatively flat, with minimal slope toward the north and northwest. Elevations at the site range from 639 to 642 feet above mean sea level (amsl). The northern portion of the site is currently an open field; however, the southern portion of the site and areas to the west are wooded.

Geophysical surveys conducted during the 1996 SI, indicated that some of the debris remains in the subsurface, as confirmed by the excavation of metallic debris during exploratory trenching. Excavated debris was described as piping, strapping, and plates. Additional soil descriptions recorded during the trenching include reference to black cinder, ash, metal objects, broken tiles, tile fragments, and broken ceramics. The soil descriptions indicate the presence of a burn layer defined as black cinder and ash,

ranging from 0.9 to 1.4 feet below ground surface (bgs) with thicknesses ranging from 0.5 to 1.2 feet. The soil descriptions for the overlying surface material indicate that the burning ground was covered with backfill material of unknown origin.

The drainage ditch is located less than 100 feet north of the former burn area and drains to the west across the site, then northwest to Pipe Creek. This drainage feature is approximately four feet wide and two to three feet deep. During a site reconnaissance in November of 2003, water was present in the ditch at an average depth of approximately 6 to 12 inches.

1.2.2 Site Geology

The 2BG site is situated on unconsolidated lacustrine deposits of glacial origin consisting of loamy fine sand and sand. These deposits range in thickness from 10 to 20 feet, based on soil borings located to the south, southwest, and west of the site. The Plumbrook Member of the Olentangy Shale subcrops beneath these unconsolidated deposits over the entire site. The estimated thickness of this shale at the site is from 20 to 30 feet, based on monitor well borings installed southwest of the site, that are generally parallel to the site in terms of bedrock strike. Thickness of the Plumbrook Shale should increase to the southeast and decrease to the northwest. The Plumbrook Shale is described as a blue, soft, fossiliferous shale containing thin layers of dark, hard, fossiliferous limestone. The Delaware Limestone underlies the Plumbrook Shale and averages 75 feet 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 the site has not been characterized; however, there is sufficient information from the *2002 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. Numerous monitoring wells have been installed adjacent to areas of known contamination during previous investigations. Sufficient water level data was collected during 2000 and 2001 to establish groundwater elevation contours for the northwestern portion of the PBOW. Based on the contour maps provided in the 2002 groundwater report, shallow groundwater elevations ranged from 636 to 639 feet amsl in May 2002, and 631 to 634 feet amsl in November 2002. Surface elevations at the site range from 639 to 642 feet amsl. Therefore, depths to shallow groundwater are expected to range from 3 to 6 feet during the wet season and 8 to 11 feet during dry season. Shallow groundwater flow is toward the north-northwest.

Groundwater elevation contours for the Delaware Limestone indicate a linear feature running northeast-southwest through the PBOW, which is acting 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. The 2BG site is located approximately 500 ft northwest of this feature, causing bedrock groundwater to flow southeast, opposite of the shallow groundwater.

1.3 SITE-SPECIFIC DEFINITION OF PROBLEMS

Chemical data obtained during the 1996 SI indicate that the surface and subsurface soil have been contaminated with semi-volatile organic compounds (SVOCs), primarily nitroaromatics, PAHs, and PCBs originating from the disposal and incineration of PBOW waste materials. Contamination levels exceed the RBCs for several compounds. Exploratory trenches revealed a fairly continuous burn layer beneath the site with associated waste debris. Samples of the burn layer were not collected as part of the 1996 SI. Subsurface soil samples collected from borings were taken from two intervals: 2 to 3 ft. bgs and 6 to 7 ft. bgs. The burn layer was observed between 0.5 and 1.4 bgs. It is unknown if this material could serve as a source of contamination. The 1996 SI identified the need for further investigation to define the nature and extent of soil contamination and to evaluate potential impacts on groundwater beneath the site and on surface water and sediment in the nearby drainage ditch. 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

Resumes of key Jacobs personnel working on this project are presented in Appendix I. The key Jacobs person responsible for project planning, control, and execution of the CAP is the Jacobs Project Manager. The Jacobs Project Manager is Mr. Virgil Jansen who is also the Program Manager. Additional key personnel include: the Technical Lead and Site Manager, Mr. Al Hardesty; the Project Chemist, Mr. Mike Houck; the Data Manager, Mr. Dave Greenberg; the Program/Project Quality Manager, Mr. Marty Alewine; the Site Safety Officer, Mr. Sean Healey; the Technical Reviewer, Mr. Steve Lampkins; and the Safety and Health Manager, Mr. Sid McNair. The duties and responsibilities associated with these key Jacobs project positions are outlined in the Quality Control Plan (QCP) (Jacobs, 2004c).

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 as a subcontractor to Jacobs, for several of the field activities.

3.0 SCOPES AND OBJECTIVES

3.1 TASK DESCRIPTION

Investigations to be conducted at 2BG include the characterization of groundwater, soil, sediment, and surface water. Project objectives include the following:

- Evaluate and use existing data appropriate to the Area of Concern (AOC)
- Define site physical features and characteristics
- Determine nature and extent of contamination in soil and groundwater at the AOC
- Determine chemical characteristics of contamination
- Evaluate fate and transport of contamination
- Determine depth, extent, and nature of the soil burn layer
- Determine presence or absence of site impact on the drainage feature bounding the north side of the AOC
- Determine whether overburden groundwater underlying the AOC is of sufficient volume to be defined as a potential drinking water source in the State of Ohio
- 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 the AOC has been evaluated by Jacobs and considered for development of project data quality objectives (DQOs). Existing data collected at the site includes analytical results from surface and subsurface soil samples, lithologic descriptions of subsurface soil collected from borings and exploratory trenches, and geophysical interpretations of the site. Existing groundwater data is available from adjacent AOCs and is useful for estimating shallow and deep groundwater elevations and gradients at the site. This data has been considered for development of the groundwater sampling strategies.

This existing data can be used to meet some of the project objectives. Information obtained from the exploratory trenches is useful for defining the type of material, depth, and thickness of the burn layer within the interior of the former burning ground. JE has reviewed the completeness and quality of the 1996 data set and found that it should meet specific data needs for a future risk assessment.

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 includes representatives from the U.S. Corp of Engineers, Ohio EPA, PBS, and Jacobs.

3.2.1 Conceptual Site Model

Based on available site information, contaminants associated with the former burning ground operations have, at a minimum, impacted the soil beneath the burn layer and surface soil at the site. Backfill placed over the burning ground was either contaminated prior to placement or was cross-contaminated during the grading process. Surface soil to the west of the burn area has also been impacted from prior operations or from regarding activities, which may have spread the contamination outside of the burn area boundary.

Existing data collected during the 1996 SI indicates surface and subsurface soil contamination exceeding RBCs for nitroaromatics, PCBs, and various metals. In general the highest concentrations of nitroaromatics are found at the surface within the boundary of the former burn area. Nitroaromatic concentrations are observed to decrease with depth within the burn area. Of the four locations sampled outside of the burn area, two contained nitroaromatics, which was limited to the surface soil only.

PCBs were found in the surface soil at all locations within the boundary of the burn area and at two locations outside of the burn area. Only one location had PCB contamination in the subsurface, which was at the 2 to 3 ft. interval, and was within the boundary of burn area.

Soil contamination for metals exceeding both the RBCs and established background values is limited to lead, aluminum, and thallium. The lead contamination is limited to surface soil and was found at one location inside the burn area and one location outside of the burn area. The aluminum exceedances are limited to the 6-7 ft. interval and was found inside the burn area at two locations. The thallium exceedances were found at 6 of the eight locations at numerous depth intervals, however in all cases the concentrations were minimally above background values.

Additional contaminant migration processes may have occurred at the site, impacting groundwater, surface water and sediment. These potential processes will be evaluated during this investigation. Potential 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 to the north into the nearby drainage system. Shallow groundwater flow paths are toward the north-northwest. Bedrock flow paths at the site are toward the southeast. Potential surface water and sediment contamination may have occurred from shallow groundwater recharge to the drainage system or by overland flow and transport of contaminated soil particles during heavy precipitation.

3.2.2 Problem Statement – Step 1

Soil samples collected during the 1996 Site Investigation (SI) were screened against the EPA Region III Risk Based Screening Criteria (RBCs). Soil contamination exceeding RBCs is present at the site. Potential contaminant source material is present at the site, represented by the cinder and ash layer and the associated debris, which may be contributing to further contaminant migration. It is unknown whether site contaminants have migrated to groundwater, surface water, and sediment. Neither the lateral extent of the burn layer nor the spatial distribution of contaminants in soil has been adequately defined.

3.2.3 Decision Statements – Step 2

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

- Determine the lateral extent of the soil burn layer.
- Determine whether the burn layer serves as a source of contamination contributing to migration of contaminants.
- Further define the lateral and vertical extent of soil contamination.
- 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, flow direction, and groundwater classification.
- Determine whether shallow and bedrock groundwater has been impacted by site contaminants.
- Determine whether surface water and sediment in the drainage ditch has been impacted by site contaminants.

3.2.4 Decision Inputs – Step 3

The majority of the decision inputs will 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 IX Preliminary Remediation Goals (PRG) for soil and established site-wide background values for inorganics in soil will be used to evaluate whether the extent of soil contamination has been adequately defined. These PRGs are discussed in Section 3.2 of the Site Wide Field Sampling Plan FSP (SWFSP) (Jacobs 2004). The extent of soil contamination will be considered adequately defined when contamination levels are below PRGs will be used as a screening tool to evaluate the site. Delineation of site contaminants will follow the approach used at the TNT Areas A,B, and C. At the conclusion of this investigation, additional sampling will be determined and negotiated based on the initial findings and the results of the risk assessment. Tables 3-3 through 3-8 of the Site-Specific Quality Assurance Project Plan (QAPP) present the PRGs to be

used for the soil investigation.

EPA Region IX PRGs for groundwater and established site-specific background values for organics and inorganics in groundwater will be used to evaluate whether additional investigation of site groundwater is warranted. Background values for certain organic compounds in the bedrock aquifer have been established at the site because of the naturally occurring oil present in the Delaware Limestone. These PRGs are addressed in Section 3.2 of the SWFSP (Jacobs 2000). Tables 3-9 through 3-14 present the PRGs to be used for the groundwater investigation. Groundwater background values will be included in the Final Site-Specific QAPP tables as they become available.

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 and MDLs for the contracted laboratories are compared to PRGs in Tables 3-3 through 3-14 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 must be obtained to perform a statistically based risk assessment. The number of samples needed for adequate site characterization to support a feasibility study must be considered.

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 2001 and 2002 site-wide groundwater study (Shaw 2002) Perimeter trenches will be located based on interpretation of aerial photography and results from previous sampling at the site. 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, Appendix F and G of the Site Investigation Report (IT 1997). Evaluation of these data and determination of their usefulness greatly affects the sampling strategies and locations for additional soil data.

3.2.5 Study Boundaries – Step 4

The 2BG site has some natural spatial boundaries related to the soil investigation, consisting of the service road immediately east of the site and the drainage ditch immediately to the north (Figure 3-1). These features form natural study boundaries. Burn activities would not have taken place in the roadway and contaminants would not be expected to cross a drainage divide.

The vertical boundary for the delineation of soil contamination will be defined as the vadose zone, consistent with EPA, DQO Process for Hazardous Waste Sites, adjusted for seasonal fluctuation.

Additional boundary issues relate to the location and size of the former burn area. The location of the burn area is based on aerial photography. It is possible that the size of the burn area varied over time based on operational needs. Because of this uncertainty, exploratory trenches to be performed as part of this investigation may need to be

extended at certain locations to fully delineate the boundaries of a soil burn layer. Likewise, soil boring locations designed for characterization of soil outside of the burn area may warrant relocation based on observations during trenching.

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. Investigation activities will be conducted during the wet season when shallow groundwater levels are typically high.

Practical constraints on data collection include trenching operations in the wooded area in the southern portion of the site. Clearing and grubbing of transect lines for obstructions such as large trees would not be practicable. Trenches will either go around obstructions or be resumed on the opposite side. Delineation control within 5 to 10 feet is sufficient to support the feasibility study.

3.2.6 Decision Rules – Step 5

Placement of soil borings will be dependant on the boundaries of the burn layer, to be defined during perimeter trenching. If the boundary of the burn area should be different than the current estimate then the boring locations will be adjusted appropriately. This may include utilization of the alternate borings as additional perimeter borings.

The decision to install shallow groundwater monitoring wells is dependant on sufficient thickness of overburden coupled with sufficient groundwater, which will be determined by the placement of five temporary peizometers. If there is not sufficient overburden or shallow groundwater levels are not sufficient, then locations for the shallow monitoring wells will be evaluated and discussed with USACE – Nashville District.

3.2.7 Decision Errors – Step 6

Decision errors for this investigation primarily relate to the delineation of soil contamination outside of the burn layer and the level of characterization required within the interior. The probability of a decision error would be greatly reduced by applying a relatively tight sampling grid over the entire site; however, such an approach would not be an efficient use of government funds, nor is it necessary to adequately characterize the site.

The risk of making a decision error regarding the land outside of the burn area and potentially missing significant contamination would be more costly than including an area of clean soil within the burn area for future remedial action. The land within the burn area is definable, while the areas outside become less so. A limited number of additional samples within the interior of the burn area can sufficiently reduce the uncertainty, whereas significantly more samples are needed outside of the burn area boundary in order reduce uncertainty.

3.2.8 Design Optimization – Step 7

The soil investigation has been subdivided into five populations for sampling design purposes:

- Burn layer material
- Surface soil inside of the burn area boundary
- Subsurface soil inside of the burn area boundary
- Surface soil outside of the burn area boundary
- Subsurface soil outside of the burn area boundary

The sampling design optimization will include the following elements:

- Exploratory trenches will be excavated to delineate the boundary of the burn area and to characterize the nature of contaminants in the burn layer.
- The soil sampling strategy and locations will be based on delineation of the burn area boundary based on results from the exploratory trenching.
- Lithologic borings and piezometers will be installed after trenching to further define the conceptual site model before collection of samples for analysis.
- Co-located surface and subsurface soil samples will be collected from borings installed within the burn area to further characterize the nature of contaminants and vertical extent.
- Co-located surface and subsurface soil samples will be collected from borings placed outside of the burn area to delineate the impacted area.
- Surface soil samples will be collected to delineate the impacted area west of the site.
- Monitoring wells will be installed in both the overburden material and bedrock, to allow for sampling and evaluation of impacts to groundwater.
- Co-located surface water and sediment samples will be collected from the drainage ditch north of the site.

3.3 APPLICABLE REGULATIONS/STANDARDS

These 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 will include the following components:

Draft Work Plans	05 March 2004
Final Work Plans	05 May 2004
Field Investigation	1 June 2004 – 14 July 2004
Sample Analysis	15 July 2004 – 14 August 2004
Draft Site Char. Soil, Sediment, and Surface Water	12 October 2004

Quarterly GW Report – Round 1	12 October 2004
Quarterly Groundwater Monitoring	05 October 2004 – 12 October 2004
Sample Analysis (2nd Qtly GW Sampling)	13 October 2004 – 12 November 2004
Quarterly GW Report – Round 2	10 January 2005
Complete All Tasks	26 February 2005

4.0 NONMEASUREMENT DATA ACQUISITION

Nonmeasurement data acquisition for this investigation includes the use of existing data collected from prior investigations at the various AOCs within the PBOW. Analytical data from soil samples collected at 2BG during the 1996 SI are intended for use in the risk assessment for the 2BG site. The electronic data and the associated Data Summary Report has not yet been obtained or reviewed. Thorough review of data will be completed to determine if the data are of compatible quality to be incorporated with data from this investigation. If the data are not acceptable, sampling designs will need to be adjusted accordingly.

5.0 INVESTIGATION METHODOLOGIES

This chapter describes the methodologies and procedures to be followed for the Remedial Investigation, Part 1 at 2BG. The investigations activities will include:

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

Sampling locations for these activities are presented in Figure 5-1 and Figure 5-2.

5.1 GEOPHYSICAL SURVEYS

Geophysical surveys are not planned as part 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 2BG PBOW to acquire data relative to groundwater level, groundwater flow, hydraulic conductivity, and impacts related to site contaminants. This investigation will include the installation of five temporary piezometers and the installation, development, and collection of groundwater samples from three overburden wells and three bedrock wells.

5.3.1 Monitoring Well Installation and Development

Five temporary piezometers will be installed at the site (Figure 5-1) following delineation of the burn area and before the soil investigation commences. These piezometers will help to define the vertical boundaries of the soil study, as defined by the depth to the water table. The piezometers will also be used to evaluate the feasibility of installing permanent shallow monitoring wells. Piezometers will be placed outside of the burn area to avoid additional migration pathways for site contaminants.

Borings for the piezometers will extend to the top of bedrock 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. No annular materials will be used for well completion other than a bentonite surface plug to minimize infiltration of surface water. Large diameter bentonite pellets will be used for this purpose. Precautions will be taken to ensure that surface completion materials do not get introduced down hole and interfere with the well screen. 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 5 to 6 weeks 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). Groundwater data for the PBOW were reviewed to evaluate whether existing monitoring wells could be used for upgradient comparisons. The nearest upgradient shallow wells are located at TNT Area C approximately 1600 ft south of the site. Groundwater collected from monitoring well TNTC-MW06 contained explosives compounds exceeding the screening criteria. The well is located considerably further than is desired, is not directly upgradient, and the presence of contaminants above screening criteria makes this well unsuitable for up-gradient purposes. Other nearby shallow wells at TNT Area C are likewise contaminated and are not directly upgradient of 2BG.

Bedrock wells in the Acid Area #2 and West Red Water Ponds Area represent the closest upgradient wells. Monitoring wells PB-BED-MW14, AA2-BEDGW-001, and PB-BED-MW19 are located 2700 to 3500 feet from the site. Groundwater samples from these wells contain explosive compounds, nitroaromatics, and SVOCs above screening criteria, which makes them unsuitable for upgradient comparisons.

Based on this evaluation, new monitoring wells will be used for upgradient comparisons. 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 burn area. Co-located wells will be placed within 10 to 25 ft of each other. Upgradient and downgradient locations are based on water level contour maps provided in the 2002 Groundwater Data Summary and Evaluation Report, which are also shown on Figure 5-1 of this document.

Borings for bedrock wells 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. Overburden wells will also be continuously sampled for lithologic characterization, with screen placement covering the best water-yielding zone nearest the surface. Screen lengths will be sized to fit a single discreet water bearing interval and will not exceed 10 feet in length, as specified in the *State of Ohio, Technical Guidance for Well Construction and Groundwater Protection, Appendix VI, Monitroing 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" in diameter larger than the

casing diameter to allow for 2' of filter pack and annular material on all sides of the screen and casing. Boreholes for shallow wells will be advanced with 6.25" 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 feet and will be spaced at 20 foot intervals. Centralizers will not be placed closer than 10 feet above the screened interval. All well materials will be placed using cased-hole methods

Well locations may be adjusted within a radius of 100 feet to account for significant differences in shallow groundwater flow directions. If adjustments are made, well pairs should not be moved beyond a point that the deep well is no longer upgradient or down gradient 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 should be given to disassociate the two wells. However, the shallow and deep wells in the center of the site should remain co-located. Decisions to change locations beyond 100 ft. or to disassociate the well pairs will be made by the DQO planning team. If changes are needed, newly acquired site information will be provided for decision making prior to beginning well installation activities, which should provide the planning team one week to make location decisions.

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 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 permanent wells on a quarterly basis (every three months) prior to sampling activities. Temporary piezometers will be measured every other day during field activities until stabilization has occurred.

5.3.3 Groundwater Sampling

Groundwater samples will be collected from newly installed wells in accordance with the SWSAP. Samples will be analyzed for target compound list (TCL) volatile organic compounds (VOCs), PAHs, target analyte list (TAL) metals, and nitroaromatics. Samples will be collected quarterly (every three months) for a minimum of two rounds. 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 burn area.

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

Five exploratory trenches will be excavated before any soil sampling is initiated (Figure 5-2) Trenches will be placed perpendicular to the interpreted boundary and will be initiated 15 ft. inside of the burn area and proceed outward until reaching the end of the burn layer. Trenches will be deep enough to characterize the full thickness of the burn layer and to visually inspect the upper 12 inches of the underlying soil. Trenches will be spaced 50 to 75 ft apart to allow for adequate boundary delineation. One trench should be sufficient on the east side of the burn area since the extent of prior burning operations was limited by the presence of the service road.

Representative samples of the burn material will be collected from each trench and analyzed for VOCs, PAHs, nitroaromatics, TAL metals, PCBs, and dioxins/furans. In an effort to minimize the disturbance of the area, pilot holes may be advanced with a shovel or hand auger to verify the presence of the burn layer, prior to initiating trenching. Trenching and sample collection will be collected in accordance the SWSAP.

Soil borings will be conducted at the site using DPT methods for the collection of subsurface soil samples (Figure 5-2). Soil borings will be conducted after trenching activities and piezometer installation activities have been completed. Boring locations will be dependant on delineation of the burn area. Locations shown on Figure 5-2 may be adjusted based on the trenching results.

Borings will extend to the top of the water table and samples will be collected 3 to 5 ft. bgs and from the interval just above the water table, not to exceed 10 feet bgs. If the overburden shows significant variability in thickness and lithology based on the five piezometer borings, select soil borings for soil sampling will extend to the top of bedrock to further develop the conceptual site model. All soil borings and sample collection will be conducted in accordance with the SWSAP.

Three borings will be advanced in the interior of the burn area to provide adequate data for the risk assessment and to evaluate the vertical extent of contamination beneath the burn layer. All samples will be analyzed for VOCs, PAHs, nitroaromatics, TAL metals and PCBs. The samples from 3 to 5 ft. will also be analyzed for dioxins/furans.

Seven borings will be advanced outside the perimeter of the burn area, placed 25 ft. from the boundary. Borings will be spaced approximately 50 to 75 ft apart at the mid point between trenches to provide additional confidence in the delineation of the burn area. If burn layer materials are encountered during any of these borings, drilling should be suspended and offset locations should be placed 25 feet further out from the burn area. The original boring location will be staked and surveyed for boundary definition.

Borings on the north and northwest side of the burn area will be placed closer together to provide additional coverage in the down gradient direction. All samples will be analyzed for VOCs, PAHs, nitroaromatics, and TAL metals. Samples collected from the 3 to 5 ft. interval will also be analyzed for PCBs.

Two additional soil borings will be reserved as alternates to further characterize soil in the down gradient direction or to maintain spacing should the burn area be larger than anticipated. If these borings are installed as shown on Figure 5-2, samples will be analyzed for VOCs, PAHs, nitroaromatics, and TAL metals. If the two alternate borings are needed for delineation of the burn area the standard suite of analysis will be performed, which will include PCBs from the 3-5 ft. interval.

Surface soil samples will be co-located with all soil borings. Samples will be collected from 0 to 1 feet bgs in accordance with the SWSAP. Samples will be analyzed for VOCs, PAHs, nitroaromatics, PCBs, and TAL metals. Surface soil samples collected inside of the burn area will also be analyzed for dioxins/furans. Additional surface soil samples will be collected west of the burn area to determine the extent of surface contamination detected at 2BGSO-07 and 2BGSO-08. These samples will be analyzed for VOCs, PAHs, nitroaromatics, PCBs, and TAL metals.

5.5 SURFACE WATER AND SEDIMENT SAMPLING

Co-located surface water and sediment samples will be collected from the drainage ditch north of the site (Figure 5-1). Sample locations include an upstream sample and two downstream samples prior to convergence with any other surface water tributaries. All sampling locations will be at least 100 to 200 feet apart. Samples will be collected during baseflow conditions, no sooner than 48 hours following any precipitation events. All samples will be collected in accordance with the SWSAP.

Surface water samples will be analyzed for VOCs, PAHs, nitroaromatics, PCBs, and TAL metals. Sampling will occur during baseflow conditions and no sooner than 48 hours following any precipitation events. Sediment samples will be analyzed for VOCs, PAHs, nitroaromatics, TAL metals, PCBs, and dioxins/furans.

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 in accordance with the SWSAP.

6.0 FIELD OPERATIONS DOCUMENTATION

Field documentation will 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 SSQAPP 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 manufactures 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. JEs vendor will be Scientific Sales Inc, out of Oak Ridge, Tennessee.

9.2 SAMPLING APPARATUS AND FIELD INSTRUMENTATION

The following equipment will used during this investigation:

- Horiba or YSI flow-thru cell
- Horiba or YSI calibration fluid
- PH buffer solution
- Peristaltic pump (surface water sampling – nonVOC)
- Grundfos Redi-Flo2 pump and reel
- Grundfos Redi-Flo2 s1/MP1 Converter with case
- Water level indicator
- Teflon coated disposable tubing
- Stainless steel well slug
- In-situ well datalogger – 1" diameter
- Generator
- Extension cords
- Five gallon buckets with lids
- Core boxes
- Munsel chart
- 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 (PPE): 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

Dames & Moore, 1996, *Site-Wide Groundwater Investigation Draft Report, Plum Brook Ordnance Works, Sandusky, Ohio*, May 1996.

Dames & Moore, 1995, *Records Review Report, Plum Brook Ordnance Works, Sandusky, Ohio*, April 27, 1995.

IT Corporation (IT), 1997, *Site Investigations of the Reservoir No. 2 Burning Ground, Additional Burning Ground, Waste Disposal Plant No. 2, and Power House No.2 Ash Pit, Former Plumbrook Ordnance Works, Sandusky, Ohio*, December 1997.

Jacobs, 2004, *Sitewide Sampling and Analysis Plan*, February 2004

Jacobs, 2004, *Sitewide Safety and Heath Plan*, February 2004

Shaw Environmental, Inc., 2003, *2002 Groundwater Data Summary and Evaluation Report, Former Plumbrook Ordnance Works*, June 2003.

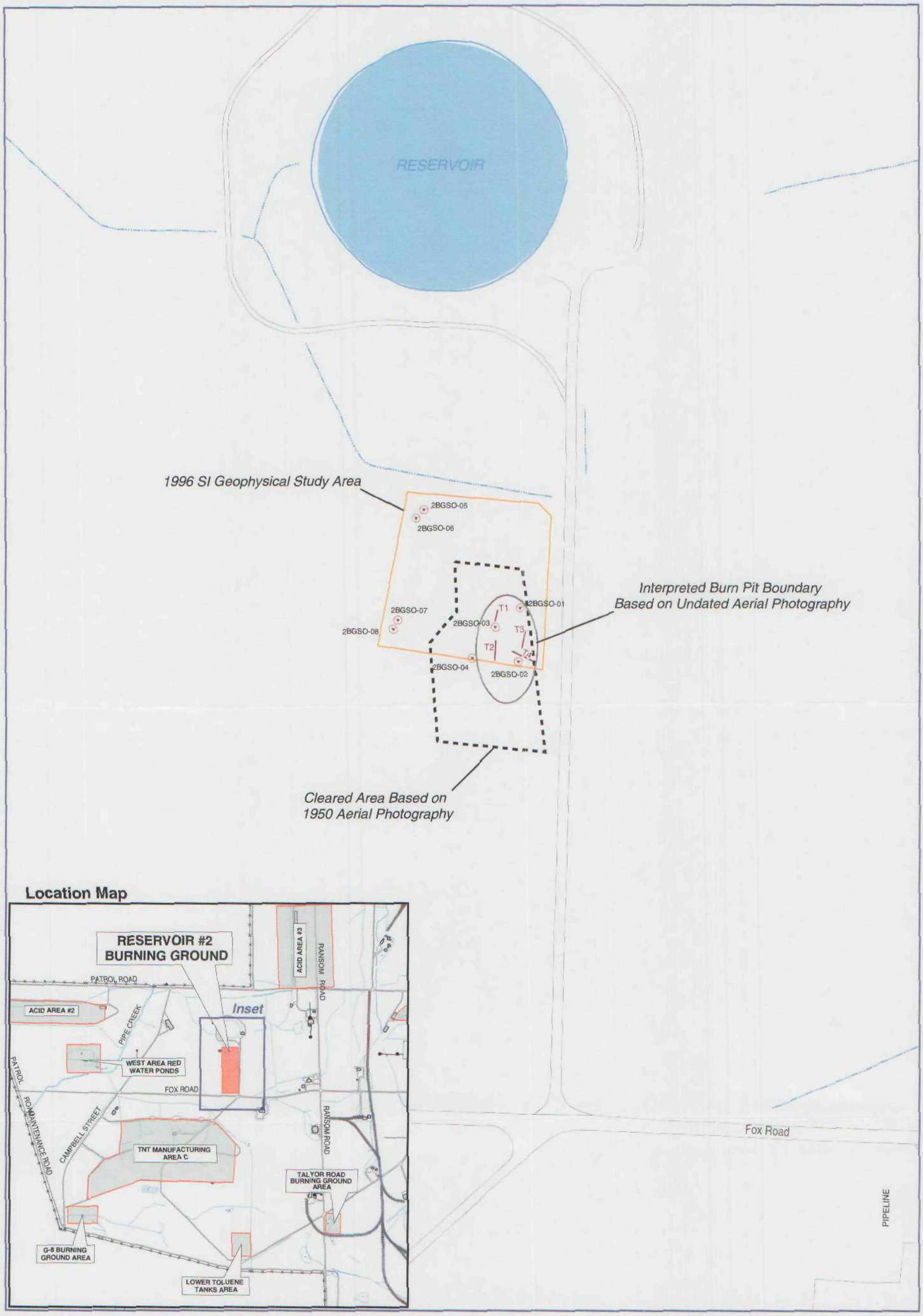
State of Ohio, *Technical Guidance for Well Construction and Ground Water Protection*, 2000

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



Area of Detail

Legend

Interpreted Burn Pit Boundary Based on Undated Aerial Photography

Cleared Area Based on 1950 Aerial Photography

1996 SI Geophysical Study Area

T2 Exploratory Trenches—1996 SI

Soil Boring—1996 SI

Creek, Ditch, Conveyance

N W E S

0 75 150
Feet

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

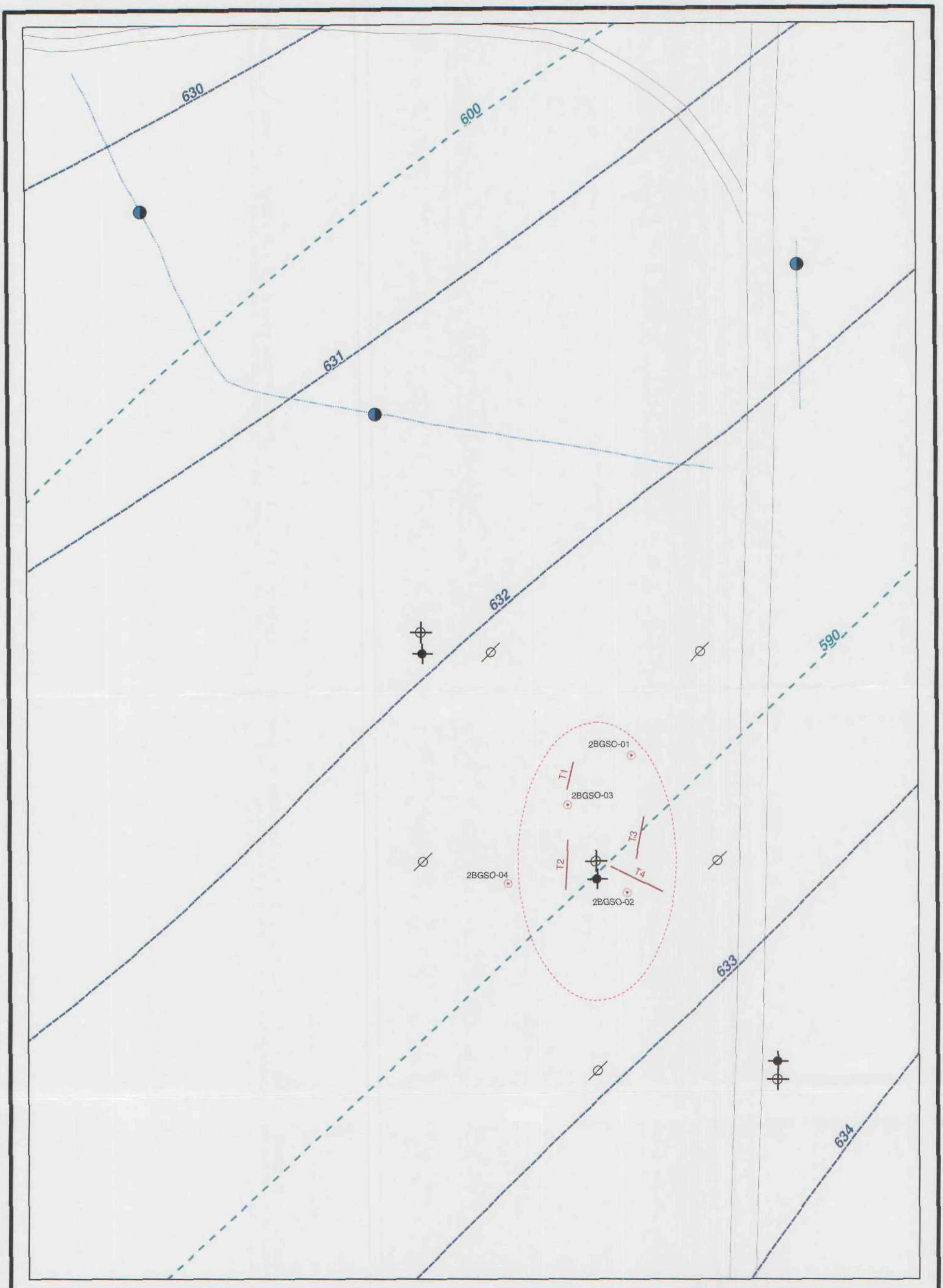
JACOBS

Interpreted Boundaries and 1996 SI Sampling Locations

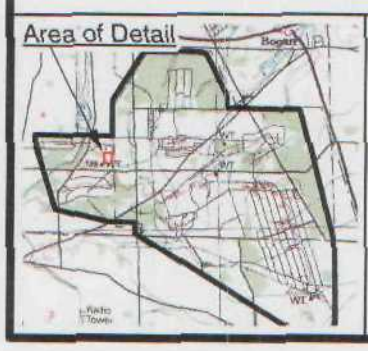
Plum Brook Ordnance Works
Sandusky, Ohio

03/16/04 NZ Y:/GIS/PlumBrook/Projects/FSP_Reservoir No. 2 Burning Ground/ArcGIS/Fig1-1_Interpreted_Boundaries.mxd

Figure 1-1



Area of Detail



Legend

- Bedrock Groundwater (Delaware Limestone) Elevation Contours—May, 2002 (feet above Mean Sea Level)
- Overburden Groundwater Elevation Contours—Nov, 2001 (feet above Mean Sea Level)
- Proposed Shallow Monitoring Well
- Proposed Surface Water Sediment Sample
- Proposed Bedrock Monitoring Well
- Proposed Temporary Piezometer
- T2 Exploratory Trenches—1996 SI
- Soil Boring—1996 SI
- Creek, Ditch, Conveyance

N W E S

0 25 50
Feet

Notes: *Data mapped to Ohio Stateplane North NAD83, map grid units in feet.*

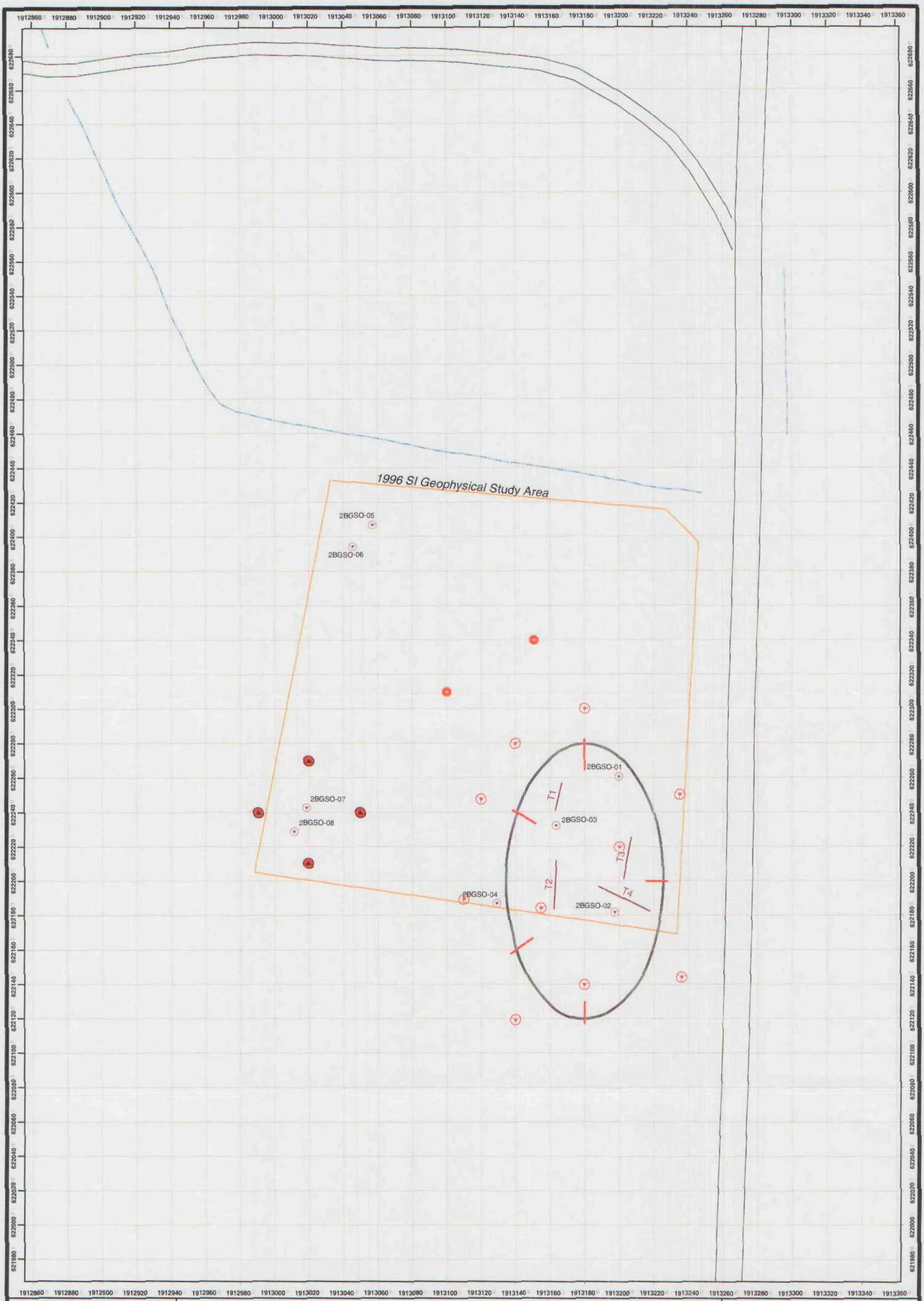
JACOBS

Groundwater, Surface Water, and Sediment Sample Locations

Plum Brook Ordnance Works
Sandusky, Ohio

03/04/04 NZ Y:/GIS/PlumBrook/Projects/FSP_Reservoir No. 2 Burning Ground/ArcGIS/Fig5-1_GW_SW_Sed_locs.mxd

Figure 5-1



Area of Detail

Legend

- Proposed Soil Borings
- Additional Downgradient Soil Borings (TBD)
- T2 Exploratory Trenches—1996 SI
- Creek, Ditch, Conveyance
- Proposed Surface Soil Sample
- Proposed Exploratory Trenches
- Soil Boring—1996 SI

N W E S

0 25 50
Feet

Notes: *Data mapped to Ohio Stateplane North NAD83. map grid interval = 20 feet.*

JACOBS

Proposed Soil Boring, Exploratory Trench, and Surface-Soil Sampling Locations

Plum Brook Ordnance Works
Sandusky, Ohio

03/04/04 NZ Y:/GIS/PlumBrook/Projects/FSP_Reservoir No. 2 Burning Ground/ArcGIS/Fig5-2_Boring_Trench_locs.mxd

Figure 5-2

14 April 2004

SUBJECT: Response to review comments for the Field Sampling Plan portion of the Site-Specific Sampling and Analysis Plan, Remedial Investigation, Part 1 at Reservoir Number 2 Burning Ground (2BG), Former Plum Brook Ordnance Works, Sandusky, Ohio, Prepared by Jacobs Engineering Group, Inc., Dated March 2004

Reviewer – CELRN – Becky Terry

1. **Page 1-1, Section 1.0, First Paragraph, Last Sentence. Figure 1-2 has been omitted from the Figures. Please provide.**

   Response: The reference to Figure 1-1 and Figure 1-2 is in error. The text should reference only the 2BG location map, which is included as Figure 1-1.

2. **Page 1-1, Section 1.0, Second Paragraph. An amendment to the QAPP has also been prepared as part of the FSP. Add a statement to this effect.**

   Response: Reference to the Site-Specific QAPP will be included.

3. **Page 1-1, Section 1.1, First Paragraph, Last Sentence. Edit. "Former" is used three times in this sentence.**

   Response: The second use of the word "former" will be deleted.

4. **Page 1-2, Section 1.1, Last Paragraph, Last Sentence. Suggest this sentence be changed. While background values for the four metals identified were not available in 1996, they have since been calculated. These values are located in Table 2-7 of the TNT Area B Risk Assessment (Shaw, August 2000).**

   Response: The updated inorganic background values have been received and reviewed. The text will be revised to read as follows: "Inorganic contaminants in surface and subsurface soil exceeding both the RBCs and the established background values are limited to lead, aluminum, and thallium". The last sentence will be deleted.

5. **Page 1-2, Section 1.2.1, 1st Sentence. I am not sure that a burn pit existed at the site. After reviewing the analytical results from the 1996 SI, it appears the highest levels of contamination were detected in the upper 0-0.5' horizon of soil. Perhaps we need to verify whether we have any evidence of a pit being present and change the SAP accordingly. I almost believe based on further discussing in this section this area was backfilled and regarded during the construction of the softball fields.**

Response: The following paragraph in this section discusses the soil descriptions collected during the trenching and soil boring activities. The four trenches and three soil borings located within the estimated boundary of the burn pit consistently have a layer of material described as cinder, ash, and burn debris. There are also historic photographs which document the burning of waste debris at this area. Three of the soil borings in this area had subsurface soil contamination exceeding RBCs for nitroaromatics. Outside of this area RBC exceedances are limited to surface soil. Jacobs proposes no changes to this section.

6. **General Comment. Please label the main roads located to the east and south of the site.**

   Response: Fox Road will be added to the figure. The access road to 2BG is not named on any of the base maps. A larger inset map will be used to show Campbell Rd, Maintenance Rd, and Ransom Rd in relation to the site.

7. **Page 2-1, Section 2.1, Second Paragraph, First Sentence. Edit this sentence. The field activities should be conducted according to the FSP. The SSHP should be used to determine safety requirements.**

   Response: The intent of this statement is to reference the SSHP and ensure that all safety procedures are followed, however the text will be rewritten as follows "All field activities will be conducted in accordance with this Site-Specific FSP and the requirements of the SSHP submitted under separate cover."

8. **Page 3-1, Section 3-1, Fifth bullet. Evaluation of contamination fate and transport was not included in the SOW.**

   Response: The bullet should remain, since data to be collected must eventually support this task. Maintaining fate and transport as one of the objectives will ensure that the investigation strategy will be sufficient for future evaluation.

9. **Page 3-1, Section 3.2, Second Paragraph. Trenches will also be used to delineate the extent of contamination.**

   Response: This section is referring to data collected during the 1996 investigation. The trenching data does not support delineation since they were placed within the interior of the burn pit.

10. **Page 3-1, Section 3.2, 2nd Paragraph, 2nd Sentence. I am concerned about the data needs being tentatively developed without reviewing the historical data. Is this to say the SI report wasn't reviewed during the development of the sampling strategy? What about some comparison of the inorganic analytical results with the background presented in the already cited risk assessment? What about the general characteristic of nitroaromatic contaminant concentration to decrease with**

increasing depth? All of this type of information would be useful in planning the data collection effort.

Response: Jacobs performed a thorough review of the available data and based the investigation on the existing data set. This sentence needs clarification. It should say "...without reviewing the raw data and evaluating the data quality for incorporation into the risk assessment." Jacobs has since received the EDD from Shaw and will make a determination on the usability of the data for the risk assessment for the Final SAP. If the data quality is not sufficient for the risk assessment, the sampling strategy may need to be revised.

11. **Page 3-2, Section 3.2.3. and 3.2.6. Expect an IF: THEN type statement.**

Response: If:Then statements are generally reserved for Step 5; Decision Rule. Step 2: Identify the Decision, is a series of statements based on linking the study questions and the alternative actions. Table 2 of the Data Quality Objectives Process for Hazardous Waste Site Investigations, EPA QA/G-4HW, page 21, shows examples of decision statements, which do not contain if:then statements.

The decision rules provided in section 3.2.6 will be rewritten to provide a more clear if:then statement. Also an additional decision rule will be added to address the alternate sample locations (see comment 13)

12. **Page 3-6, Section 3.2.8. First bullet. Insert the installation of the five pizometers.**

Response: Piezometer installation is discussed in the third bullet on the previous page.

13. **Page 5-4, Section 5.4, Next to Last Paragraph, Last Sentence. Explain and edit.**

Response: the sentence will be revised as follows: If the two alternate locations are needed for delineation of the burn pit, the standard suite of analysis will be collected which includes PCBs from the 3-5 ft. interval as discussed in the preceding paragraph.

14. **Page 5-5, Section 5.4, Last Paragraph, Last Two Sentences. Please delete these sentences.**

Response: This discussion will be removed.

15. **Page 5-5, Section 5.4, Last Paragraph. Why are no subsurface samples being collected in the vicinity of 2BGSO-08 and 2BGSO-07?**

Response: The 1996 data indicates no subsurface soil contamination outside of the burn pit boundary. The contamination west of the burn pit was limited to surface soil only. Also we are limited to 45 soil samples.

16. **Page 6.1, Section 6.0. Will daily Quality Control Reports be submitted?**

Response: Yes. QCRs are addressed in section 9.0 of the Site-Wide SAP.

17. **Page 7-1, Section 7.0. Please provide a table with the sample containers, preservatives and holding times for each analytical method. Also provide a table with the all samples collected and that will be analyzed for each method. Provide the matrix and the QA/QC samples that will be collected for easy reference.**

    Response: Agreed. The summary Tables 3-1 and 3-2 of the Site-Specific QAPP will be referenced in this section.

18. **Page 9-1, Section 9.2. Provide the documentation and calibration procedures and for the PID/FID.**

    Response: This is provided in Jacobs Work Instruction WI-039, Organic Vapor Measurement, which will be provided in the Final Site-Specific SAP.

19. **Page 10-1, Section 10.0. If a nonconformance is noted for a piece of field equipment during the field work, have arrangements been made for another instrument to be shipped on site within 24 hours? Who is the vendor that will provide these services?**

    Response: Yes. If a piece of equipment is not functioning properly it is routine for Jacobs vendors to overnight a replacement. Jacobs supplier will be Scientific Sales Inc, out of Oak Ridge, Tennessee

Subject: Response to review comments for the Site-Specific Sampling and Analysis Plan, Remedial Investigation, Part 1, At Reservoir No. 2 Burning Ground (2BG), Former Plum Brook Ordnance Works, Sandusky, Ohio, March 2004, prepared by Jacobs Engineering.

Reviewer Name: Groenjes, Cheryl (Chemistry) – HTRW Center of Expertise

Comment # 1: General. I worked with CRREL recently on an explosives module for the Field Analytical Technology Encyclopedia (FATE) website cosponsored by the Corps and EPA; and have gleaned a few facts from this to share FYI and in support the Site-Specific Definition of Problem presented in section 1-3 and proposed sampling efforts described in sections 3.2.5, 3.2.6. and 5.4. Heat from the burning process sometimes resulted in melting of the energetic material, which penetrate below the surface at burning grounds and resolidify - leading to sometimes pure material in the shallow subsurface. I have attached a picture of subsurface re-crystallization of explosives found between burning trays at an ordnance works facility. Note: The orange-colored soil at the bottom of the pit contains percent levels of TNT. Visual observations should be documented clearly to allow accurate interpretation of sample data, and it's link back to the CSM for the identification of potential sources within the 2BG.

Response: Jacobs has proposed to excavate to 12" below the burn layer and provide visual descriptions of the burn layer and soil beneath the burn layer. Prior trenching performed at the site in 1996 did not identify any pure explosive product, however the reviewers comment is noted and appreciated. Jacobs will carefully observe the soil beneath the burn layer.

Comment # 2: p. FSP 3-5, 3.2.7. Suggest the adoption of field analytics (for nitroaromatics) in an adaptive sampling / analytical strategy to reduce decision error for this site. These techniques can provide general information on a larger number of samples. The greater sample density affords more effective information site-wide for the identification of potential contaminant hot spots outside of the burning pit boundary (currently stated as a decision error that cannot be mitigated due to budget constraints). An integrated analytical strategy provides more information site-wide, and allows the focusing of samples for offsite analyses to locations appropriate for its intended use - i.e., where samples should be taken to support the risk assessment. This approach will be more cost effective for the samples sent for more costly analysis are more meaningful in light of the measurements obtained in the field. Although the field measurements are not typically used within the risk assessment, the information is critical in developing an accurate CSM, and interpreting the fewer (more costly analytical) data. Several techniques, i.e., colorimetric-based, would be able to provide the information needed to focus contingency analyses by the definitive methods.

Response: This approach was not included in the SOW. Such an approach would result in fewer fixed laboratory samples and an increased percentage of drilling costs if used for subsurface delineation. This approach may be appropriate for surface soil hot spots during a subsequent phase of investigation if the risk assessment suggests further action is warranted. Jacobs experience with field test kits for delineation purposes have not been positive, frequently yielding false positives and thus incurring unnecessary stepouts.

Comment # 3: p. FSP 5-3, 1st paragraph. Suggest the use of a project website to communicate issues amongst team members.

Response: A project website does exist, however not all information is available due to security issues.

Comment # 4: QAPP pgs. 3-1 – 3-3, 3.1.1 The analytical protocols designated for surface and subsurface soils is incomplete and in error for the following. It should be noted that different prep methods perform differently. In order to maintain continuity in data obtained to support site characterization, suggest ensuring the protocols noted are complete and documented within the record. Suggest checking with your laboratories to ensure what they will be using to ensure consistency in data obtained between the primary and QA labs also. Update protocols given within each area as follows:

a. Method 3540C is the currently promulgated method for soxhlet.

b. Method 8082 (PCBs) requires the designation of a preparation method.

c. Method 6010C and 7000 series methods for metals requires the designation of a preparation method (typically 3050 or 3051)

Response: Agree. The corrections and additions will be made as requested.

Comment # 5: p. QAPP 3-3, 3.1.2. Due to the discussion covering both SW and sediments, analytical protocols should designate preparatory procedures for both water and soil matrix-types. For instance, VOCs by 8260B in water should require the use of 5030B as an appropriate preparation method. Method 8310 for PAHs in water could use 3510C or 3520C. Regardless, the sample should be analyzed at the pH received. PCBs and metals needs both water and soil prep methods identified. Refer to SW-846 Chapter 2 for further details.

Response: Agree. The appropriate prep methods will be designated for each matrix and analysis.

Comment # 6: p. QAPP 3-4, 3.1.3.

a. The sample handling proposed for the dissolved metals samples is not recommended, and has been shown to induce a low bias in the dissolved metals data. Suggest filtration be done in the field as soon as possible to ensure the validity of the data and avoid rejection of, or suspicion of low bias in the data by the regulatory authority.

b. The preparatory methods included here for VOCs and PAHs do not apply to GW – but are designed for soils. Replace or include appropriate preparatory methods for VOCs, PAHs, and metals.

Response: a) Agree. The text will be amended to indicate that the samples will be filtered in the field.

b) Agree. The prep methods will be amended to reflect the appropriate matrix.

Comment # 7: p. QAPP 3-5, 3.1.4. After the TCLP procedure (1311) is complete, the leachate undergoes a preparation method prior to IDW analyses much like a water sample does. Suggest including the appropriate preparatory method within the analytical protocols.

Response: Agree. The preparatory methods will be added to the text.

Comment # 8: p. QAPP 3-5, 3.2.1. Suggest a review of the SI data be done to identify an initial group of Chemicals Of Potential Concern (COPCs), and then evaluate whether sensitivity for those COPCs is sufficient for the intended comparison to screening values (RBCs). Those COPCs that do not meet sensitivity requirements should be clearly identified and decisions made whether method modifications are possible, needed and then pursued. There are several ways to increase a method' sensitivity. For instance, a larger volume of sample can be processed (i.e., VOCs can undergo a 25 mL purge vs. the 5 mL used, use larger soils sub-samples), the extract can be reduced down further, or an alternative procedure can be chosen that is more amenable to these techniques, etc. However, these types of measures must be coordinated with the lab and focused to improve the usability of critical data points and COPCs only. Suggest these planning issues be fully resolved prior to finalization of this SS-SAP to ensure data generated meets its intended purposes as much as possible prior to the shipment of samples to the lab.

Response: The current scope of work defines the required analytical methods for the investigation, which is the target analyte and target compound list as defined in the QAPP. SW-846 analytical methods have been selected to achieve the lowest sensitivity for the analytes and compounds. The draft SSQAPP does identify the compounds where the standard analytical methods will not achieve the Region III screening levels for the standard method lists of target compounds. The current QAPP approach is to handle the uncertainty between the Region III screening criteria and laboratory reporting levels as part of the risk assessment (for the compounds with higher reporting levels than the screening criteria).

Comment # 9: p. QAPP table 3-1. Some of the prep methods are incorrect – i.e., designate a method designed for soils to the water. Edit for consistency with the changes proposes with sections 3.1.1 to 3.1.4.

Response: Agree. The table will be edited to add prep methods and verified for consistency with Sections 3.1.1 to 3.1.4.

Comment # 10: p. QAPP table 3-2 Suggest the use of the 25g Encore sampler as the container for the TCLP VOC sample. The corrosivity (pH) method for liquid IDW should be changed to 9040B if the waste is anticipated to be aqueous in nature. Method 9045C should be retained if it is a waste (organic-based) media.

Response: Agree. The changes will be made as requested.

Comment #11: p. QAPP tables 3-9 through 3-14.

a. Suggest updating the units for the correct matrix and ensure the RBC values represent the correct media for a comparison to GW and SW.

b. Refer to comment 8 as it pertains to the additional planning necessary to compare those highlighted compounds (showing inadequate sensitivity) with the initial list of COPCs based on the existing SI data review. Suggest method modification needs be evaluated and

discussed with appropriate laboratory POCs to optimize data generated as useful for its intended purpose.

Response: a) The erroneous units will be corrected.

b) Jacobs acknowledges the comment. (see response to comment #8). The uncertainty for the compounds that have sensitivity levels greater than the Region IX PRGs will be handled in the risk assessment.

Comment # 12: p. QAPP table 3-15.

A. The acceptance criteria noted here are oversimplified for the sake of brevity. However, the following does not represent what is presented within the EPA SW-846 methods or the Shell for Analytical Chemistry Requirements (Appendix I) of EM 200-1-3. Method 8260B ICAL is not compliant with 8260B 7.3.6.2 and Shell I.9.2.2. CCC only evaluation is not correct – must be all target analytes for ICAL. The use of the mean %RSD or mean %D requires additional documentation and constraints as noted in the last paragraphs of I.9.2.2. Suggest the adoption of footnotes or other means to ensure compliance.

b. Method 8330 must be modified slightly to detect and quantitate for PETN. The same extract is used, however, the UV wavelength for PETN detection is at 210nm, and the remainder of the nitroaromatics are monitored at 254nm as established within the method. These are not typical method options addressed within the method. Therefore these details must be addressed within the appropriate QAPP documents.

Response: a) The table will be expanded to fully list the requirements of the methods and the Shell document.

b) PETN is not currently a target analyte for this site. If the scope changes to include the need for analysis of PETN, the modifications will be added to the site specific QAPP.

Reviewer Name: Crain, Mike (Geology) - HTRW Center of Expertise

Comment # 1: Field Sampling Plan, 5.3.1, pg 5-2, 1st par – Some consideration should be given to making a couple of the piezometers permanent to permit future monitoring of shallow groundwater flow directions. The arrangement of the permanent monitoring wells parallel to the direction of groundwater flow makes sense from the standpoint of monitoring contaminant concentrations. Unfortunately, this arrangement will not allow the direction of groundwater flow to be measured. The flow direction that is measured initially in the temporary piezometers may change with seasonal fluctuations in groundwater levels. If the piezometers to the west and northeast were made permanent, that would provide an adequate network of measurement points to monitor changes in groundwater flow.

Response: The temporary piezometers are to be used solely for collecting preliminary water level information to determine the feasibility of installing permanent overburden wells. Any additional use of the piezometers will discussed with the OEPA.

Reviewer Name: Charles G. Coyle (Env Engineer) – HTRW Center of Expertise

Comment # 1: p. 3-3, 3.2.4 It is noted that the text indicates that naturally occurring oil is present in the Delaware Limestone. This could represent a potential sink for partitioning and immobilization of organic contaminants in groundwater.

Response: The comment is acknowleged. This information will be retained for site evaluations during the investigation reporting.

Comment # 2: p. 5-3, 5.4 This section indicates that soil boring samples will be collected from the surface and vadose zone locations. However some soil boring samples should also be collected from locations in the saturated zone, as explained below. This section or the section on installation of monitoring well installation (5.3.1) should be revised to require that some soil boring samples be collected. Data on TOC levels (in groundwater, soil from the aquifer matrix, and also from sediments), will be important from a natural attenuation perspective (especially with regard to adsorption and irreversible binding of nitroaromatics, see Haderlein, S.B., Schwarzenbach, R.P; Environmental Processes Influencing the Rate of Abiotic Reduction of Nitroaromatic Compounds in the Subsurface. In: «Biodegradation of Nitroaromatic Compounds», J.C. Spain (Ed.). Plenum Press, New York 1995, pp.199-225. [1993). Recommend revising to to require that some soil boring samples be collected from vadose zone locations that have been impacted by nitroaromatics.

Response: The comment is acknowledged. The SOW and budget is based on a maximum of 45 soil samples, which have been judicially selected to provide the greatest amount of site characterization. These additional samples could be evaluated for later investigations following the performance of the site risk assessment.

RE: NASA Plum Brook Station
Erie County

April 29, 2004

United States Army Corps of Engineers
Nashville District
Attn: CELRN-EP-R-M (Ms. Linda Ingram)
Estes Kefauver Federal Building
801 Broadway
Nashville, Tennessee 37202-1070

Dear Ms. Ingram:

Please find below the response to comments for the commentary of the Ohio Environmental Protection Agency (Ohio EPA) with respect to the Site-Specific Sampling and Analysis Plan (SAP), Remedial Investigation, Part 1 at Reservoir No.2. Burning Ground, Former Plum Brook Ordnance Works as well as the corresponding Site-Specific Quality Assurance Project Plan (QAPP).

1. General Comment

The SAP references the use of site-specific background samples; however, it does not distinguish whether said background data is specific to the No. 2 Burning Grounds or indicative of the data obtained from the Site-Wide Background study. Please note that the collection and use of site-specific background information should be discussed in this SAP. Site-specific background can be used in addition to the United States Environmental Protection Agency (USEPA), Region IX Preliminary Remediation Goals (PRGs) when screening site data for naturally occurring inorganic compounds. If Site-Wide Background Data is available, please provide a table that summarizes the values used to represent background.

Response: No site-specific background characterization was intended. This investigation will utilize the previously established values from the Site-Wide Background Study. Further clarification will be included in the text.

2. SAP Section 3.2.2

The text discussing the extent of soil contamination should be revised to indicate that "extent" will be defined when contamination levels are below risk based concentrations or background, whichever value is lower.

Response: Delineation of site contaminants will follow the approach used at the TNT Areas A,B, and C. At the conclusion of this investigation, additional sampling will be determined and negotiated based on the initial findings. The objective of this initial investigation is not to fully and accurately define the extent of contamination exceeding RBCs. The third bullet in Section 3.2.3 will be revised to read "Further define the lateral and vertical extent of soil contamination".

3. SAP Section 3.2.2
This section should be revised to state that soil contamination exceeding USEPA Region IX "PRGs" not "RBCs" is present at the No. 2 Burning Grounds.

Response: The 1996 Site Investigation Report for the site used risk-based screening criteria based on EPA Region III tables, 1996. This statement is simply defining the results of the prior investigation and should not be changed.

4. SAP Section 3.2.4
The Site-Specific SAP states that ground water analytical data will be evaluated against background values and USEPA Region III Tap Water or residential risk-based concentrations (RBCs). Background ground water values will be provided in a final version of the Site Specific SAP when they become available. Ohio EPA is not amenable to the above approach of standards comparison. Ohio EPA recommends the use of USEPA Region IX PRGs as the primary source of risk based screening values. The Site-Wide SAP, which details general investigatory methodologies and/or protocols, states that ground water analytical data will also be compared to USEPA drinking water maximum contaminant levels (MCLs). In general, MCLs are "Applicable or Relevant and Appropriate Requirements" (ARARs) and, as such, are not considered appropriate as risk based values for the screening of constituents of concerns in ground water. Therefore, if background values are not available for comparative purposes upon initiation of Part I of the remedial investigation (RI) at Reservoir No.2. Burning Ground, USEPA Region IX PRGs should be used.

Response: Screening criteria for groundwater will be revised to reflect the use of Region IX PRGs. Site-Wide background values for groundwater should be established and ready for comparison purposes during preparation of the investigation report.

5. SAP Section 5.3.1
The remedial investigation proposes the installation of five temporary overburden piezometers around the periphery of the Reservoir No.2. Burning Ground, in part, to determine shallow ground water flow . The SAP states that the piezometers shall be constructed such that no annular materials will be utilized and a bentonite surface plug will be installed to reduce surface water infiltration. This section should be revised to specify whether the annular space will consist of in-situ (natural formation) material or some other material. Please note that precautions should be undertaken to ensure that the bentonite pellets will not reach the screened interval of the well.

Response: This section will be revised to clarify that no annular material will be introduced other than bentonite pellets for the surface seal. Additional procedures will be included to ensure that the bentonite pellets are contained at the upper 18" of the annulus and do not impact the well screen.

6. With respect to the installation of three nests of overburden and bedrock monitoring wells,

this section should be revised to note the material and dimensions of the shallow and deep monitoring wells (i.e., 2-inch, PVC, 4-inch stainless steel, etc.).

Response: The section will be revised to include the requested information.

7. The section should be revised to reference the Site-Wide SAP for the development and sampling of the proposed piezometers and monitoring wells at Reservoir No.2. Burning Ground.

Response: The last sentence in Section 5.3.1 references the development procedures established in the SWSAP for permanent monitoring wells . The temporary piezometers are to be used solely for collecting preliminary water level information to determine the feasibility of installing permanent overburden wells. Any additional use of the piezometers will discussed with the OEPA.

8. As general reminder, the contracted laboratory must be able to achieve practical quantification limits (PQLs) or method detection limits (MDLs) which provide the lowest limit of detection for the corresponding analytical method as specified in USEPA SW-846 Methods and that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The PQLs or MDLs must be lower than the corresponding maximum contaminant levels (MCLs).

Response: The laboratory MDLs are required to be determined per 40 CFR, Part 136, Appendix B or an equivalent statistical approach. The laboratory MRLs are required to be set at the laboratory MQL (or PQL) for this project to achieve as many of the project's risk based criteria as possible. In addition the analytical subcontractors are also reporting detected concentrations of target analytes down to their MDL values qualified as estimated "J".

9. SAP Section 5.3.2
The text indicates that water level monitoring will be conducted on all permanent wells on a quarterly basis prior to sampling activities. Ohio EPA is unclear as to what 'quarterly' means as well as which permanent wells will be measured. Typically, Ohio EPA interprets 'on a quarterly basis' as four events per year. Clarification should be provided as to whether only the newly installed permanent wells will be checked or all overburden and bedrock monitoring wells will be checked.

Response: Clarification will be provided to indicate that only the newly installed permanent wells at the 2BG site will be monitored. Clarification will be given as to the use of "quarterly", which refers to every three months or four times per year.

10. SAP Section 5.3.3
Clarification should be provided regarding the following sampling strategy: "samples will be collected quarterly for a minimum of two rounds". As previously noted, Ohio EPA typically associates "quarterly" with four discrete events. This section of the SAP as well as the Site-Specific Quality Assurance Project Plan should be revised incorporating the appropriate clarification.

Response: Funds are available for the collection of two rounds of data. Additional rounds will be funded at a later date and the number of rounds needed will be discussed with OEPA.

11. SAP Section 5.3.4
The SAP states that slug testing will be performed on all permanent monitoring wells. This section should be revised to state that all newly installed shallow and bedrock monitoring wells at the Reservoir No.2. Burning Ground will be slug tested to eliminate any ambiguity.

Response: The text will be revised to specify that the permanent wells include three shallow overburden and three bedrock monitoring wells. Slug testing will not be performed on temporary piezometers.

12. SAP Section 5.4
Sampling depths for surface soil should be consistent with the exposure intervals that will be defined and evaluated in the Risk Assessment. Surface soil is typically defined as the interval between 0 and 1 foot or 0 and 2 feet. Please note that "defining" the surface soil interval in this manner is consistent with the approach used in previous risk assessments associated with the former Plum Brook Ordinance Works. Under the residential exposure scenario, the subsurface soils interval may extend to a depth of 13 feet. This section should be revised to ensure that sampling intervals are consistent with previous investigations and clearly identify what depth interval is considered surface soil as opposed to subsurface soil.

Response: The text will be revised to expand the surface soil interval to include 0 to 12 inches bgs. Jacobs will remove the text regarding ten feet being the lower limit for exposure scenarios. The deep sampling interval will remain as stated, either the two foot interval above the water table or the 8 to 10 foot interval. This approach will be consistent with prior investigations at the site.

13. Since polychlorinated byphenols (PCBs) are considered a potential contaminant of concern, dioxins/furans should also be incorporated into the list of analytes for the laboratory to evaluate.

Response: Dioxins/furans are called out in the text and are associated with all trench samples, all surface soil samples inside the burn pit boundary, and the subsurface samples from 3 to 5 feet within the burn pit boundary. Funds are available for collecting 15 samples for dioxin/furan analysis. Additional sampling as needed will be evaluated at the conclusion of this investigation.

14. QAPP Section 3.1.3
The Site-Specific QAPP states that dissolved metals samples will only be collected during the initial round of ground water sampling at the six new monitoring wells at Reservoir No.2. Burning Ground. These samples will be shipped to the laboratory unpreserved and unfiltered where the laboratory will perform these activities. It is the position of Ohio EPA that ground water samples collected for dissolved metals analyses should be preserved and filtered in the field. Ground water may undergo immediate changes upon extraction from the monitoring

well. By requesting filtering from the laboratory, the sample has potentially several hours of residence time where the chemistry of the sample can vary thus rendering it unrepresentative of actual aquifer conditions. Dissolved metals ground water samples should be field filtered with a 0.45 micron inline filter.

Response: Agreed. Jacobs will amend this section of the QAPP to include field filtration of the dissolved metals samples.

15. Clarification should be provided regarding the following sampling strategy: "samples will be collected quarterly for a minimum of two rounds". As previously noted, Ohio EPA typically associates "quarterly" with four discrete events. This section of the SAP as well as the Site-Specific Quality Assurance Project Plan should be revised incorporating the appropriate clarification.

Response: Currently only two quarterly groundwater sampling events are scoped at a duration of three months apart. Additional rounds will be funded at a later date and the number of rounds needed will be discussed with OEPA.

16. The Site-Specific SAP should provide for the generation of separate piezometer, shallow (overburden), and bedrock potentiometric surface maps. Ground water surface elevations collected from piezometers and shallow (overburden) monitoring wells should not be combined into one map due to their differences in construction, installation, and development.

Response: The temporary piezometers are to be used solely for collecting preliminary water level information to determine the feasibility of installing permanent overburden wells. Any additional use of the piezometers will discussed with the OEPA.

QAPP

FINAL SITE-SPECIFIC QUALITY ASSURANCE PROJECT PLAN

REMEDIAL INVESTIGATION, PART 1, RESERVOIR NUMBER 2 BURNING GROUND (2BG)

FORMER PLUM BROOK ORDNANCE WORKS SANDUSKY, OHIO

Prepared for:

DEPARTMENT OF THE ARMY
NASHVILLE DISTRICT, CORPS OF ENGINEERS
NASHVILLE, TENNESSEE
CONTRACT DACW62-03-D-0004-0002

Prepared by:

JACOBS ENGINEERING GROUP, INC.
125 BROADWAY
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May 2004

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LIST OF ACRONYMS AND ABBREVIATIONS

CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
CQAR	Chemical Quality Assurance Report
EPA	U.S. Environmental Protection Agency
ft	foot
GEL	General Engineering Laboratories, LLC
GPL	GPL Laboratories, Inc.
HTRW-CX	Hazardous, Toxic, Radioactive Waste Center of Expertise
IDW	investigation-derived wastes
MDL	method detection limit
MRL	method reporting limit
NFG	USEPA National Functional Guidelines for Data Review
PAH	polynuclear aromatic hydrocarbon
PCB	polychlorinated biphenyl
PM	Project Manager
QAPP	Quality Assurance Project Plan
QA	quality assurance
QC	quality control
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
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
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 Remedial Investigation, Part 1 Reservoir Number 2 Burning Ground Sampling and Analysis Plan (SAP). This SSQAPP is an addendum to the Site Wide QAPP (Jacobs 2004) prepared as part of the Former Plum Brook Ordnance Works Site Wide Sampling and Analysis Plan (SWSAP), and 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 Remedial Investigation, Part 1, Reservoir Number 2 Burning Ground 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, Nashville District (USACE). Jacobs has prepared this QAPP under Contract No. DACW62-03-D-0004, Task Order Number 0002.

The U. S. Army Corps of Engineers (USACE) EM-200-1-3, *Requirements for the Preparation of Sampling and Analysis Plans* (Feb. 2001), 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.

General Engineering Laboratories (GEL) will provide analytical support as the primary laboratory. They will perform all primary analyses with the exception of the dioxin and furan, PCB and PAH analyses at their Charleston, South Carolina facility. GEL will subcontract the primary dioxin and furan analyses to Paradigm Analytical Laboratories, Inc. in Wilmington, North Carolina. GEL will subcontract the primary PAH and PCB analyses to Ecology and Environment, Inc. in Lancaster, NY.

GPL Laboratories, Inc. (GPL) will provide analytical support as the Quality Assurance (QA) laboratory. They will perform all QA analyses with the exception of the dioxin and furan analysis at their Gaithersburg, Maryland facility. GPL will subcontract the QA dioxin and furan analyses to PACE Analytical Services in Minneapolis, Minnesota.

GEL, Paradigm, GPL, and PACE have been evaluated by the USACE HTRW-CX and hold current letters of validation from HTRW-CX to perform sample analyses in support of the USACE HTRW-CX Program. 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 USACE validation letters are contained in Appendix A.

The laboratory contacts are as follows:

Jake Crook, Project Manager (PM)
General Engineering Laboratories
2040 Savage Road
Charleston, SC 29414
Phone: 843-556-8171 Fax: 843- 766-1178

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Paradigm Analytical Laboratories, Inc.
2627 Northchase Parkway S.E.
Wilmington, NC 28405
Phone: 919-552-0044
Fax: 910-350-1557

Alan Laffin
Ecology and Environment, Inc.
Analytical Services Center
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Lancaster, NY 14086
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Deborah Griffiths
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Frederick, MD 21703
Phone: 301-694-5310
Fax: 301-620-0371

Scott Unze, PM
PACE Analytical Services
1700 Elm Street
Suite 200
Minneapolis, MN 55414
Phone: 612-607-6383

1.1 ANALYTICAL LABORATORY PROJECT MANAGER

The GEL and GPL Project Mangers, Jake Crook and Debbie Griffith 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. The GEL and GPL Project Managers are also responsible for coordinating with their subcontract analytical laboratories such that it appears seamless to Jacobs that analyses are subcontracted. Section 1.1 of the Site Wide QAPP (Jacobs 2004) provides greater detail on the analytical Project Managers' responsibilities.

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

Robert Pullano and Elsa Tai are the QA/QC Directors at GEL and GPL, respectively, and are identified as such on the laboratory organizational charts in Appendix B of this QAPP. Section 1.2 of the Site Wide QAPP provides greater detail on the analytical QA/QC Directors' responsibilities.

1.3 ANALYTICAL LABORATORY TECHNICAL MANAGERS

Pat Steele and Yamane Yohannes are the analytical subcontractor Technical Managers, (the organics and inorganics Group Supervisors) for GEL and GPL Laboratories, respectively. They are identified as such on the laboratory organizational charts in Appendix B of this QAPP. Section 1.3 of the Site Wide QAPP provides greater detail on the analytical laboratory Technical Managers' responsibilities.

2.0 DATA ASSESSMENT ORGANIZATION AND RESPONSIBILITIES

Refer to Section 2.0 of the Site Wide QAPP.

2.1 PRIMARY SAMPLE DATA ASSESSMENT

Section 2.1 of the Site Wide QAPP presents the three-step data review process. Third-party data validation is not required for this investigation.

2.2 QA SAMPLE DATA ASSESSMENT

The QA sample data will be evaluated and compared to the associated primary sample results by Stratum Engineering, Inc. Stratum Engineering will be under subcontract to Jacobs, but will perform the evaluation of the QA data, comparison to the primary data, and write the Chemical Quality Assurance Report (CQAR) independent of Jacobs. GPL and PACE, the QA analytical subcontractors, will report the QA sample results directly to Stratum Engineering. GPL and PACE will be responsible for the same internal data review procedures as the primary laboratories, as detailed in Section 8.1 of the Site Wide QAPP, for 100% of the QA data prior to submittal to Stratum Engineering. Jacobs will be responsible for providing the primary data to Stratum Engineering for comparison to the QA data. The results of the QA data review and evaluation against the primary results will be documented in the Chemical Quality Assurance Report (CQAR) prepared by Stratum Engineering. The data assessment and CQAR will be prepared per the requirements of USACE-HTRX-CX, EM-200-1-6 *Chemical Quality Assurance for HTRX Projects,* October 1997.

The QA assessment firm contact is:

Filippe B. Cade, P.E.

Stratum Engineering, Inc.
3751 Pennridge Drive
Suite 119
Bridgeton, MO 63044
Phone: (314) 739-1987

3.0 DATA QUALITY OBJECTIVES

Section 3.0 of the SSFSP (Jacobs 2004) provides the investigation objectives and data needs for the Remedial Investigation at 2BG.

3.1 DATA USE BACKGROUND

The specific data needs for 2BG have been developed based on the existing Site Investigation (SI) performed by Shaw Environmental, Inc. (formerly IT Corporation) in 1996. 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 define the nature and extent of contamination at 2BG. Forty-five total soil samples will be collected from surface, subsurface, and trenching locations. 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 Site Wide QAPP (Jacobs 2004). 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 of this QAPP 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 3-14 of this QAPP. Dioxin and furan samples will also be collected from locations where native burn material is encountered, which is expected to be present at eleven locations. The soil remedial investigation samples will be analyzed using the following analytical methods:

Trenching Subsurface Soils: five samples

- TCL Volatile Organic Compounds (VOCs) (SW-846 5035/8260B)
- Polynuclear Aromatic Hydrocarbons (PAHs) (SW-846 3540C/8310)
- Polychlrinated Biphenyls (PCBs) (SW-846 3540C/8082)
- Nitroaromatics (SW-846 8330)
- Dioxins and furans (SW-846 8290)
- TAL Metals (SW-846 3050B/6010C/7471A series)

Subsurface Soils Interior Burn Pit Area: Six samples collected from 2 depths at 3 locations from the interior burn pit area

- TCL VOCs (SW-846 5035/8260B)

- PAHs (SW-846 3540C/8310)
- PCBs (SW-846 3540C/8082)
- Nitroaromatics (SW-846 8330)
- TAL Metals (SW-846 3050B/6010C/7471A series)
- Dioxins and furans (SW-846 8290) (only 3 samples collected from 3-5 ft. interval for dioxin/furans)

Subsurface Soils Perimeter Area: 14 samples collected from 2 depths at 7 locations from the perimeter of the burn pit area

- TCL VOCs (SW-846 5035/8260B)
- PAHs (SW-846 3540C/8310)
- Nitroaromatics (SW-846 8330)
- TAL Metals (SW-846 3050B/6010C/7471A series)
- PCBs (SW-846 3540C/8082) (only 7 samples collected from 3-5 ft. interval at 7 locations for PCB analysis)

Subsurface Soils Down Gradient Area: 4 samples collected from 2 depths at 2 locations down gradient from the burn pit area

- TCL VOCs (SW-846 5035/8260B)
- PAHs (SW-846 3540C/8310)
- Nitroaromatics (SW-846 8330)
- TAL Metals (SW-846 3050B/6010C/7471A series)

Surface Soils: 12 locations co-located with the subsurface borings in the interior burn pit, perimeter, and down gradient areas

- TCL VOCs (SW-846 5035/8260B)
- PAHs (SW-846 3540C/8310)
- Nitroaromatics (SW-846 8330)
- PCBs (SW-846 3540C/8082)
- TAL Metals (SW-846 3050B/6010C/7471A series)

- Dioxins and furans (SW-846 8290) (only 3 samples co-located with the interior burn pit area borings for dioxin/furan analysis)

Surface Soils: 4 locations collected from a perimeter hot spot area

- TCL VOCs (SW-846 5035/8260B)
- PAHs (SW-846 3540C/8310)
- Nitroaromatics (SW-846 8330)
- PCBs (SW-846 3540C/8082)
- TAL Metals (SW-846 3050B/6010C/7471A series)

3.1.2 Surface Water And Sediment Sampling

Three co-located surface water and sediment samples will be collected from the drainage ditch north of the site to determine whether the operations at the burn area have impacted the drainage ditch. 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 Site Wide QAPP. The surface water and sediment samples will be analyzed using USEPA SW-846 methodology and the USEPA 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 surface water and sediment samples for each method are provided in Tables 3-3 through 3-14 of this QAPP. Dioxin and furan samples will be collected from the sediment locations only. 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)
- PAHs (SW-846 8310 with 3540C for sediments and 3520C for surface waters)
- PCBs (SW-846 8082 with 3540C for sediments and 3520C for surface waters)
- Nitroaromatics (SW-846 8330)
- Dioxins and furans (SW-846 8290) (sediments only, surface waters not analyzed for dioxin/furans)
- TAL Metals (SW-846 3050B/6010C/7471A for sediments, and SW-846 3005A/6020/7470A for surface waters)

3.1.3 Groundwater Monitoring Well Sampling

Six groundwater monitoring wells will be sampled quarterly for at least two rounds to determine any impact of the burning ground on groundwater. The purpose of the

groundwater monitoring samples is to define the nature and extent of groundwater contamination associated with the burning ground, 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 Site Wide QAPP. The samples will be analyzed using USEPA SW-846 methodology and the USEPA 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 of this QAPP 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 3-14 of this QAPP. 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)
- PAHs (SW-846 3520C/8310)
- Nitroaromatics (SW-846 8330)
- TAL Metals (SW-846 3005A/6020/7470A 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 seven IDW samples are expected to be collected. The samples will be analyzed (or subcontracted) by the transportation and disposal (T&D) subcontractor, Integrated Solutions and Services, Inc. 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 of this QAPP 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 Site Wide QAPP (Jacobs 2004) is required for the IDW sample analyses. The IDW samples will be analyzed by the following methods:

- TCLP VOCs (SW-846 1311/5030/8260B)
- TCL SVOCs (SW-846 1311/3510C/8270C)

- TAL 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 Site Wide QAPP.

3.2.1 Sensitivity

The sensitivity requirements for analytes are based on the Region IX Preliminary Remediation Goals (PRGs) for this project. The Region IX PRGs, laboratory method reporting limits (MRLs), and method detection limits (MDLs) are provided in Tables 3-3 through 3-14 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 remedial investigation activities associated with 2BG, and compares the sensitivity requirements to the actual analytical subcontractors' MRLs and MDLs for each chemical parameter of interest.

Although analytical methods have been selected to provide the highest level of sensitivity 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 3-14. 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 maximum sensitivity 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 Site Wide QAPP (Jacobs 2004) 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 2BG. Table 3-15 of this QAPP provides the laboratory precision and accuracy goals.

3.2.3 Accuracy

Section 3.2.3 of the Site Wide QAPP (Jacobs 2004) provides the field and laboratory accuracy requirements. Table 3-15 of this QAPP provides the laboratory precision and accuracy goals.

3.2.4 Completeness

Section 3.2.4 of the Site Wide QAPP (Jacobs 2004) provides the field and laboratory completeness requirements.

3.2.5 Representativeness

Section 3.2.5 of the Site Wide QAPP (Jacobs 2004) provides the field and laboratory representativeness requirements.

3.2.6 Comparability

Section 3.2.6 of the Site Wide QAPP (Jacobs 2004) provides the field and laboratory comparability requirements.

4.0 SAMPLE RECEIPT, CUSTODY, AND HOLDING TIME REQUIREMENTS

Section 4.0 of the Site Wide QAPP (Jacobs 2004) 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 standard operating procedures (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 2BG 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 3-14 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 Site Wide QAPP (Jacobs 2004) provides a discussion on the required laboratory instrument preventative maintenance.

5.3 LABORATORY CALIBRATION PROCEDURES AND FREQUENCY

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

5.4 QUALITY CONTROL REQUIREMENTS

Section 5.4 of the Site Wide QAPP (Jacobs 2004) 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 investigation at 2BG.

Acceptance criteria and/or target ranges for QC samples are provided in Table 3-15 of this QAPP for each of the required analytical methods. The criteria provided in Table 3-15 is based on Appendix I, *Shell for Analytical Chemistry Requirements* from EM-200-1-3, *Requirements for the Preparation of Sampling and Analysis Plans* (Feb. 2001), For methods not included in the *Shell for Analytical Chemistry Requirements* document, the internal laboratory limits and control ranges will be used.

5.5 PERFORMANCE AND SYSTEM AUDITS

Section 5.5 of the Site Wide QAPP (Jacobs 2004) provides a discussion on the requirements and types of audits that may be performed.

5.6 NONCONFORMANCES AND CORRECTIVE ACTIONS

Section 5.6 of the Site Wide QAPP (Jacobs 2004) provides the requirements of the nonconformance and corrective action system that the program will follow.

5.7 QUALITY ASSURANCE REPORTS TO MANAGEMENT

Section 5.7 of the Site Wide QAPP (Jacobs 2004) provides a discussion on the quality reporting system for this program.

6.0 DATA REDUCTION/CALCULATION OF DATA QUALITY INDICATORS

Section 6.0 of the Site Wide QAPP (Jacobs 2004) provides the field and laboratory data reduction procedures, and the data usability reconciliation process. Tables 3-3 through 3-14 provide the Region IX PRGs and the laboratory MRLs and MDLs for each chemical parameter of concern for the investigation at 2BG.

7.0 DATA REPORTING

Section 7.0 of the Site Wide QAPP (Jacobs 2004) 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 investigation at 2BG will be 28 calendar days from receipt of the samples.

8.0 DATA MANAGEMENT

Section 8.0 of the Site Wide QAPP (Jacobs 2004) provides the data review, verification, and validation procedures.

9.0 REFERENCES

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, February 2004. *Draft Site Wide Quality Assurance Plan, Former Plumbrook Ordnance Works Sandusky, Ohio.*

Jacobs, February 2004. *Draft 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.

TABLES

TABLE 3-1

PLUMBROOK ORDINANCE RESERVOIR NO. 2 BURNING GROUND SAMPLE SUMMARY

SAMPLE DESCRIPTION/ LOCATIONS	MATRIX	SAMPLE TYPE	ANALYTICAL PARAMETERS/ METHODS	NUMBER AND TYPE OF FIELD SAMPLES				
				Primary/ QA	Duplicate	Trip Blank[1]	MS/ MSD	Equipment Rinsate
Trenching Subsurface Soil Sampling	Soil	Grab	TCL VOCs (5035/8260B) PAHs (3540C/8310) PCBs (3540C/8082) Nitroaromatics (8330) Dioxin/Furans (8290) TAL Metals (3050B/6010B/ 7471A)	5/1	1	0	2 (1 pair)	0
Interior Burn Pit Subsurface Soil Sampling	Soil	DPT borings	TCL VOCs (5035/8260B) PAHs (3540C/8310) PCBs (3540C/8082) Nitroaromatics (8330)	6/1	1	0	2 (1 pair)	0
			TAL Metals (3050B/6010B/ 7471A) Dioxin/Furans (8290)	3/1	1	0	2 (1 pair)	0
Perimeter Area Subsurface Soil Sampling	Soil	DPT borings	TCL VOCs (5035/8260B) PAHs (3540C/8310) Nitroaromatics (8330)	14/1	1	0	0	0
			TAL Metals (3050B/6010B/ 7471A) PCBs (3540C/8082)	7/1	1	0	0	0

TABLE 3-1 (continued)

SAMPLE DESCRIPTION/ LOCATIONS	MATRIX	SAMPLE TYPE	ANALYTICAL PARAMETERS/ METHODS	NUMBER AND TYPE OF FIELD SAMPLES				
				Primary/ QA	Duplicate	Trip Blank[1]	MS/ MSD	Equipment Rinsate
Down Gradient Subsurface Soil Sampling	Soil	DPT borings	TCL VOCs (5035/8260B) PAHs (3540C/8310) Nitroaromatics (8330) TAL Metals (3050B/6010B/ 7471A)	4/0	0	0	0	0
Surface Soil Sampling (Soil samples collocated with DPT borings)	Soil	Grab	TCL VOCs (5035/8260B) PAHs (3540C/8310) PCBs (3540C/8082) Nitroaromatics (8330) TAL Metals (3050B/6010B/ 7471A)	12/1	1	0	2 (1 pair)	0
			Dioxin/Furans (8290)	3/1	1	0	2 (1 pair)	0
Surface Soil Sampling (Hot spot area west of burn pit)	Soil	Grab	TCL VOCs (5035/8260B) PAHs (3540C/8310) PCBs (3540C/8082) Nitroaromatics (8330) TAL Metals (3050B/6010B/ 7471A)	4/1	1	0	0	0
Sediment samples collected from drainage ditch North of the burning ground	Sediment	Grab	TCL VOCs (5035/8260B) PAHs (3540C/8310) PCBs (3540C/8082) Nitroaromatics (8330) Dioxin/Furans (8290) Total Metals (3050B/6010B/ 7471A)	3/1	1	0	2 (1 pair)	0

TABLE 3-1(continued)

SAMPLE DESCRIPTION/ LOCATIONS	MATRIX	SAMPLE TYPE	ANALYTICAL PARAMETERS/ METHODS	NUMBER AND TYPE OF FIELD SAMPLES				
				Primary/ QA	Duplicate	Trip Blank[1]	MS/ MSD	Equipment Rinsate
Surface water samples collected from drainage ditch North of the burning ground	Surface water	Grab	TCL VOCs (5030/8260B) PAHs (3540C/8310) PCBs (3540C/8082) Nitroaromatics (8330) TAL Metals (3005A/6020/ 7470A)	3/1	1	1	2 (1 pair)	0
Groundwater monitoring well samples	Ground-water	Grab	TCL VOCs (5030/8260B) PAHs (3540C/8310) PCBs (3540C/8082) Nitroaromatics (8330) TAL Metals (3005A/6020/ 7470A) Turbidity (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)	12/2	2	2	2 (1 pair)	1

TABLE 3-1(continued)

SAMPLE DESCRIPTION/ LOCATIONS	MATRIX	SAMPLE TYPE	ANALYTICAL PARAMETERS/ METHODS	NUMBER AND TYPE OF FIELD SAMPLES				
				Primary/ QA	Duplicate	Trip Blank[1]	MS/ MSD	Equipment Rinsate
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)	7/0	0	0	0	0

TABLE 3-2
PLUMBROOK ORDINANCE RESERVOIR NO. 2 BURNING GROUND
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
PAHs	3540C/8310	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
Dioxins/ Furans	8290	8 oz Glass	Cooled to 4±2°C	14 Days	40 Days
Metals	3050B/6010B	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)
PAHs	3520C/8310	1000 ml Amber Glass	Cooled to 4±2°C	7 Days	40 Days
PCBs	3520C/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/6020	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

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+03	1	0.83	5.0	0.88
Chloromethane	1.2E+03	1	0.37	10.0	0.97
Bromomethane	3.9E+02	1	0.5	10.0	1.07
Vinyl chloride	7.9E+01	1	0.56	10.0	0.96
Chloroethane	3.0E+03	1	0.81	10.0	1.03
Trichlorofluoromethane	3.9E+04	1	0.5	5.0	0.91
1,1,2-Trichloro-1,2,2-trifluoroethane	5.6E+06	5	2.5	5.0	0.96
Methylene chloride	9.1E+03	5	1.35	10.0	1.13
Acetone	1.6E+05	5	3.52	10.0	2.75
Carbon disulfide	3.6E+04	5	2.36	5.0	0.61
Methyl acetate	2.2E+06	10	3.3	5.0	2.72
1,1-Dichloroethene	1.2E+04	1	0.5	5.0	0.90
1,1-Dichloroethane	5.1E+04	1	0.47	5.0	1.00
cis-1,2-Dichloroethene	4.3E+03	1	0.47	5.0	0.98
trans-1,2-Dichloroethene	6.9E+03	1	0.53	5.0	0.96
Methyl tert-butyl ether	6.2E+04	1	0.53	5.0	1.06
Chloroform	3.6E+02	1	0.52	5.0	1.02
1,2-Dichloroethane	2.8E+02	1	0.43	5.0	0.96
2-Butanone	7.3E+05	5	3.74	10.0	2.36
Bromochloromethane		1	0.5	5.0	0.95
1,1,1-Trichloroethane	1.2E+06	1	0.53	5.0	0.91
Cyclohexane	1.4E+05	5	1.62	5.0	0.98
Carbon tetrachloride	2.5E+02	1	0.49	5.0	0.79
Bromodichloromethane	8.2E+02	1	0.49	5.0	0.87
1,2-Dichloropropane	3.4E+02	1	0.48	5.0	0.98
cis-1,3-Dichloropropene	7.8E+02	1	0.43	5.0	1.14
Trichloroethene	5.3E+01	1	0.45	5.0	1.10
Methylcyclohexane	2.6E+05	2	0.51	5.0	1.00
Dibromochloromethane	1.1E+03	1	0.5	5.0	0.92
1,1,2-Trichloroethane	7.3E+02	1	0.54	5.0	1.25
Benzene	6.0E+02	1	0.45	5.0	1.12
trans-1,3-Dichloropropene	7.8E+02	1	0.25	5.0	1.12
Bromoform	6.2E+04	1	0.49	5.0	0.99
Isopropylbenzene	5.7E+04	1	0.45	5.0	1.31
4-Methyl-2-pentanone	7.9E+04	5	4.03	10.0	1.36
2-Hexanone		5	3.77	10.0	1.46
Tetrachloroethene	1.5E+03	1	0.38	5.0	1.33
1,2-Dibromoethane	6.9E+00	1	0.42	5.0	1.12

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	1	0.34	5.0	1.11
1,1,2,2-Tetrachloroethane	4.1E+02	1	0.91	5.0	1.23
Chlorobenzene	1.5E+04	1	0.41	5.0	1.10
Ethylbenzene	8.9E+03	1	0.38	5.0	1.27
Styrene	1.7E+06	1	0.39	5.0	1.30
Xylenes (total)	2.7E+04	1	0.39	5.0	3.39
1,2-Dibromo-3-chloropropane	4.5E+02	1	0.75	5.0	1.27
1,3-Dichlorobenzene	1.6E+03	1	0.31	5.0	1.35
1,4-Dichlorobenzene	3.4E+03	1	0.37	5.0	1.17
1,2-Dichlorobenzene	3.7E+05	1	0.45	5.0	1.12
1,2,3-Trichlorobenzene		1	0.35	5.0	2.44
1,2,4-Trichlorobenzene	6.5E+04	1	0.36	5.0	2.30

TABLE 3-4
Soil and Sediment PAH Target Compounds

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+05	33.3	16.3	6.67	1.56
Acenaphthylene	NA	33.3	18.9	33.3	2.93
Anthracene	2.2E+06	3.33	1.19	3.33	0.44
Benzo(a)anthracene	6.2E+02	3.33	1.54	0.33	0.07
Benzo(a)pyrene	6.2E+01	6.67	2.61	3.33	0.67
Benzo(b)fluoranthene	6.2E+02	6.67	3.29	13.3	1.46
Benzo(g,h,i)perylene	NA	16.7	9.73	6.67	1.54
Benzo(k)flouranthene	6.2E+03	6.67	2.31	26.70	8.11
Chrysene	6.2E+04	16.7	8.29	0.33	0.07
Dibenzo(a,h)anthracene	6.2E+01	6.67	2.53	6.67	0.84
Fluoranthene	2.3E+05	33.3	11.6	33.3	8.44
Fluorene	2.7E+05	66.7	30.9	13.3	13.3
Indeno(1,2,3-cd)pyrene	6.2E+02	6.67	3.84	13.3	1.48
Naphthalene	5.6E+03	33.3	16.4	66.7	8.27
Phenanthrene	NA	33.3	14.1	1.67	0.28
Pyrene	2.3E+05	33.3	10.9	0.17	0.04

TABLE 3-5
Soil and Sediment PCB Target Compounds

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+02	20	15	3.3	3.69
Aroclor-1221	2.2E+02	40	24.8	33.0	15.7
Aroclor-1232	2.2E+02	20	14.3	33.0	9.9
Aroclor-1242	2.2E+02	20	12.1	33.0	4.6
Aroclor-1248	2.2E+02	20	4.1	33.0	7.0
Aroclor-1254	2.2E+02	20	14.2	33.0	7.2
Aroclor-1260	2.2E+02	20	14.9	3.3	3.17

TABLE 3-6
Soil and Sediment Nitroaromatic Target Compounds

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	375	125	100	30.1
2,6-Dinitrotoluene	7.2E+02	375	125	100	54.8
2-Amino-4,6-dinitrotoluene		375	125	100	18.9
4-Amino-2,6-dinitrotoluene		375	125	100	36.1
HMX	3.1E+05	375	125	200	50.9
m-Dinitrobenzene	6.1E+02	375	125	100	10.2
m-Nitrotoluene	3.7E+04	375	125	200	75.4
Nitrobenzene	2.0E+03	375	125	100	32.7
o-Nitrotoluene	3.7E+04	375	125	200	153.6
p-Nitrotoluene	3.7E+04	375	125	200	73.9
RDX	4.4E+03	375	125	200	76.2
sym-Trinitrobenzene	1.8E+05	375	125	200	50.9
Tetryl		375	125	200	168.3
Trinitrotoluene, 2,4,6- (TNT)	1.6E+04	375	125	100	26.2

TABLE 3-7
Soil and Sediment Dioxin and Furan Target Compounds

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)
2,3,7,8-Tetrachlorodibenzo-p-dioxin	3.9E-03	0.001	0.0009	0.001	0.0003
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	7.7E-03	0.005	0.0003	0.005	0.0003
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	9.0E-02	0.005	0.0002	0.005	0.0007
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	9.0E-02	0.005	0.0004	0.005	0.0007
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	9.0E-02	0.005	0.0005	0.005	0.0005
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	3.9E-06	0.005	0.0003	0.005	0.0008
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	3.9E-06	0.01	0.0009	0.005	0.0014
2,3,7,8-Tetrachlorodibenzofuran	3.9E-04	0.001	0.0001	0.001	0.0003
1,2,3,7,8-Pentachlorodibenzofuran	1.9E-04	0.005	0.0002	0.005	0.0003
2,3,4,7,8-Pentachlorodibenzofuran	1.9E-03	0.005	0.0002	0.005	0.0005
1,2,3,6,7,8-Hexachlorodibenzofuran	3.9E-04	0.005	0.0002	0.005	0.0004
1,2,3,7,8,9-Hexachlorodibenzofuran	3.9E-04	0.005	0.0001	0.005	0.0006
1,2,3,4,7,8-Hexachlorodibenzofuran	3.9E-04	0.005	0.0004	0.005	0.0005
2,3,4,6,7,8-Hexachlorodibenzofuran	3.9E-04	0.005	0.0004	0.005	0.0004
1,2,3,4,6,7,8-Heptachlorodibenzofuran	3.9E-05	0.005	0.0004	0.005	0.0007
1,2,3,4,7,8,9-Heptachlorodibenzofuran	3.9E-05	0.005	0.0004	0.005	0.0007
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	3.9E-06	0.01	0.0006	0.01	0.0013

TABLE 3-8
Soil and Sediment Metals Target Compound List

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+06	10	0.7931	20	1.44
Antimony	3.1E+03	1	0.3433	2.0	0.23
Arsenic	3.9E+02	0.5	0.2064	2.0	0.27
Barium	5.4E+05	0.5	0.0667	0.50	0.02
Beryllium	1.5E+04	0.5	0.0500	0.20	0.01
Cadmium	3.7E+03	0.5	0.0478	0.60	0.03
Calcium	NA	10	1.3041	100	7.30
Chromium	2.1E+05	0.5	0.1611	0.50	0.08
Cobalt	9.0E+05	0.5	0.0798	0.50	0.05
Copper	3.1E+05	0.5	0.2003	1.0	0.13
Iron	2.3E+06	10	1.5670	15	2.09
Lead	400	0.5	0.2837	1.0	0.16
Magnesium	NA	10	0.5848	25	1.42
Manganese	1.8E+05	1	0.1308	0.50	0.06
Mercury	2.3E+03	10	0.9830	0.03	0.02
Nickel	1.6E+05	0.5	0.0854	1.0	0.15
Potassium	NA	10	3.5763	25	1.89
Selenium	3.9E+04	0.5	0.1621	2.0	0.28
Silver	3.9E+04	0.5	0.0902	0.30	0.05
Sodium	NA	10	3.6314	250	9.02
Thallium	5.2E+02	1	1.0000	3.0	0.41
Vanadium	5.5E+04	1	0.0908	1.0	0.07
Zinc	2.3E+06	0.5	0.1683	2.0	0.25

TABLE 3-9
Groundwater and Surface Water Volatile 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)
Dichlorodifluoromethane	3.9E+01	1	0.43	5.0	0.84
Chloromethane	1.5E+00	1	0.5	10.0	0.67
Bromomethane	8.7E-01	1	0.5	10.0	0.46
Vinyl chloride	2.0E-02	1	0.55	10.0	0.92
Chloroethane	4.6E+00	1	0.5	10.0	1.5
Trichlorofluoromethane	1.3E+02	1	0.5	5.0	0.86
1,1,2-Trichloro-1,2,2-trifluoroethane	5.9E+03	5	2.5	5.0	0.75
Methylene chloride	4.3E+00	5	1.9	10.0	1.12
Acetone	6.1E+01	5	2.29	10.0	2.89
Carbon disulfide	1.0E+02	5	1.91	5.0	0.53
Methyl acetate	6.1E+02	5	1.45	5.0	2.15
1,1-Dichloroethene	3.4E-01	1	0.41	5.0	0.57
1,1-Dichloroethane	8.1E+01	1	0.41	5.0	0.50
cis-1,2-Dichloroethene	6.1E+00	1	0.3	5.0	0.20
trans-1,2-Dichloroethene	1.2E+01	1	0.37	5.0	0.59
Methyl tert-butyl ether	1.3E+01	5	0.32	5.0	0.17
Chloroform	5.2E-01	1	0.36	5.0	0.44
1,2-Dichloroethane	1.2E-01	1	0.29	5.0	0.36
2-Butanone	1.9E+02	5	2.31	10.0	1.15
Bromochloromethane		1	0.5	5.0	0.25
1,1,1-Trichloroethane	3.2E+02	1	0.34	5.0	0.67
Cyclohexane	3.5E+03	1	0.33	5.0	0.55
Carbon tetrachloride	1.7E-01	1	0.29	5.0	0.77
Bromodichloromethane	1.8E-01	1	0.38	5.0	0.43
1,2-Dichloropropane	1.6E-01	1	0.25	5.0	0.27
cis-1,3-Dichloropropene	4.0E-01	1	0.3	5.0	0.34
Trichloroethene	2.8E-02	1	0.36	5.0	0.46
Methylcyclohexane	5.2E+02	1	0.34	5.0	0.79
Dibromochloromethane	1.3E-01	1	0.29	5.0	0.43
1,1,2-Trichloroethane	2.0E-01	1	0.34	5.0	0.30
Benzene	3.4E-01	1	0.33	5.0	0.47
trans-1,3-Dichloropropene	4.0E-01	1	0.29	5.0	0.23
Bromoform	8.5E+00	1	0.5	5.0	0.25
Isopropylbenzene	6.6E+01	1	0.29	5.0	0.55
4-Methyl-2-pentanone	1.6E+01	5	1.78	10.0	0.36
2-Hexanone		5	1.45	10.0	0.63
Tetrachloroethene	5.6E-01	1	0.33	5.0	1.00
1,2-Dibromoethane	7.6E-04	1	0.25	5.0	0.36
Toluene	7.2E+01	1	0.39	5.0	0.36
1,1,2,2-Tetrachloroethane	5.5E-02	1	0.49	5.0	0.44
Chlorobenzene	1.1E+01	1	0.32	5.0	0.39

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)
Ethylbenzene	2.9E+00	1	0.21	5.0	0.64
Styrene	1.6E+02	1	0.25	5.0	0.34
Xylenes (total)	2.1E+01	1	0.25	5.0	1.13
1,2-Dibromo-3-chloropropane	4.8E-02	1	0.75	5.0	0.61
1,3-Dichlorobenzene	5.5E-01	1	0.33	5.0	0.29
1,4-Dichlorobenzene	5.0E-01	1	0.25	5.0	0.33
1,2-Dichlorobenzene	3.7E+01	1	0.36	5.0	0.33
1,2,3-Trichlorobenzene		1	0.32	5.0	0.88
1,2,4-Trichlorobenzene	1.9E+01	1	0.42	5.0	0.55

TABLE 3-10
Groundwater and Surface Water PAH 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)
Acenaphthene	3.7E+01	1.0	0.208	0.20	0.051
Acenaphthylene	NA	1.0	0.0824	1.0	0.131
Anthracene	1.8E+02	0.1	0.0237	0.10	0.018
Benzo(a)anthracene	9.2E-02	0.1	0.0061	0.01	0.002
Benzo(a)pyrene	9.2E-03	0.2	0.0643	0.10	0.013
Benzo(b)fluoranthene	9.2E-02	0.2	0.0171	0.40	0.057
Benzo(g,h,i)perylene	NA	0.5	0.0435	0.20	0.032
Benzo(k)flouranthene	9.2E-01	0.2	0.0434	0.80	0.089
Chrysene	9.2E+00	0.5	0.0184	0.01	0.002
Dibenzo(a,h)anthracene	9.2E-03	0.2	0.0179	0.20	0.020
Fluoranthene	1.5E+02	1.0	0.0626	1.0	0.213
Fluorene	2.4E+01	2.0	0.0802	0.40	0.045
Indeno(1,2,3-cd)pyrene	9.2E-02	0.2	0.0109	0.40	0.042
Naphthalene	6.2E-01	1.0	0.064	2.0	0.342
Phenanthrene	NA	1.0	0.0441	0.05	0.008
Pyrene	1.8E+01	1.0	0.0457	0.005	0.002

TABLE 3-11
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	0.5	0.249	1.0	0.15
Aroclor-1221	3.4E-02	1.0	0.243	1.0	0.8
Aroclor-1232	3.4E-02	0.5	0.153	1.0	0.4
Aroclor-1242	3.4E-02	0.5	0.173	1.0	0.5
Aroclor-1248	3.4E-02	0.5	0.15	1.0	0.1
Aroclor-1254	3.4E-02	0.5	0.084	1.0	0.2
Aroclor-1260	3.4E-02	0.5	0.151	1.0	0.22

TABLE 3-12
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*	0.975	0.325	0.26	0.074
2,6-Dinitrotoluene	9.9E-02*	0.5408	0.182	0.26	0.096
2-Amino-4,6-dinitrotoluene		0.975	0.325	0.26	0.129
4-Amino-2,6-dinitrotoluene		0.4862	0.1625	0.26	0.135
HMX	1.8E+02	0.4862	0.1625	0.52	0.128
m-Dinitrobenzene	3.6E-01	0.975	0.325	0.26	0.061
m-Nitrotoluene	6.1E+00	0.975	0.325	0.52	0.194
Nitrobenzene	3.4E-01	0.4862	0.1625	0.26	0.139
o-Nitrotoluene	6.1E+00	0.4862	0.1625	0.52	0.058
p-Nitrotoluene	6.1E+00	0.975	0.325	0.52	0.092
RDX	6.1E-01	0.4862	0.1625	0.52	0.395
sym-Trinitrobenzene	1.1E+02	0.975	0.325	0.26	0.051
Tetryl		1.4625	0.4875	0.52	0.092
Trinitrotoluene, 2,4,6- (TNT)	2.2E+00	0.4862	0.1625	0.26	0.086

TABLE 3-13
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+03	15	9.08	100	1.4
Antimony	1.5E+00	2.0	0.28	1.0	0.2
Arsenic	**4.5E-02**	**3**	**1**	**5.0**	**0.48**
Barium	2.6E+02	2	0.19	5.0	0.099
Beryllium	7.3E+00	0.2	0.08	0.2	0.02
Cadmium	1.8E+00	1	0.04	0.5	0.071
Calcium	NA	100	40	1,000	9.9
Chromium	1.1E+01	3	0.38	2.0	0.3
Cobalt	7.3E+01	1	0.06	1.0	0.04
Copper	1.5E+02	1	0.69	2.0	0.09
Iron	1.1E+03	25	12.584	50	3.6
Lead	NA	2	0.05	2.0	0.04
Magnesium	NA	10	6.33	100	1.6
Manganese	8.8E+01	5	1.61	2.0	0.05
Mercury	1.1E+00	0.2	0.05	0.2	0.1
Nickel	7.3E+01	2.0	0.07	1.0	0.09
Potassium	NA	300	15.06	1000	4.2
Selenium	1.8E+01	5	0.64	5.0	0.6
Silver	1.8E+01	1	0.04	0.3	0.015
Sodium	NA	250	9.68	1000	5.0
Thallium	2.4E-01	**0.5**	0.02	**2.0**	0.2
Vanadium	2.6E+01	10	5.44	5.0	1.6
Zinc	1.1E+03	10	1.09	10	0.7

TABLE 3-14
Groundwater Water Quality Analyses

Analyte	Method	Region 9 PRG (ug/L)	Primary Lab MRL (mg/L)	Primary Lab MDL (mg/L)	QA Lab MRL (mg/L)	QA Lab MDL (mg/L)
Turbidity	EPA 180.1		0.2NTU	0.1NTU	1.0	NA
Alkalinity	EPA 310.1		1	0.725	1.0	0.565
Hardness	SM 2340B		0.6615	0.03517	1.00	0.929
Total Organic Carbon	SW-846 9060		0.2	0.025	1.0	0.24
Total Dissolved Solids	EPA 160.1		10	3.067	10	3.9
Total Suspended Solids	EPA 160.2		5	0.7638	5.0	1.53
Chloride	EPA 300.0/325.3		0	0.0322	0.50	0.272
Total Cyanide	SW-846 9010A/9012	7.3E+02	5	1.7181	0.005	0.002
Nitrate	EPA 300.0/353.2	1.0E+04	0.1	0.0341	0.05	0.025
Sulfate	EPA 300.0/375.4		0.4	0.193	1.0	0.19

Table 3-15
PLUMBROOK ORDINANCE RESERVOIR NO. 2 BURNING GROUND
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 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 8310 PAHs	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%

Table 3-15 (continued)

Analysis	QC Check	Acceptance Limits
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
SW-846 7470A/7471A Mercury	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	80% to 120%
	Matrix Duplicate	≤ 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
Laboratory HTRW-CX Certifications

General Engineering Laboratories
Inter Office Correspondence

Date: December 1, 2003

To: Certification File

From: Robert L. Pullano/Director, Quality Systems

Subject: Army Corps HTRW Center of Expertise

Note to file.

GEL has been contacted by the Laboratory Validation Coordinator of the HTRW for information to continue GEL's validation status. GEL's validation expiration date is February 8, 2004. The process will take a few months and during that time GEL can continue to support the U.S. Army Corps of Engineers environmental programs.

Please contact the Laboratory Validation Coordinator (402) 697-2574 at the Corps if any there are any questions on this continued status.

DEPARTMENT OF THE ARMY
CORPS OF ENGINEERS
HTRW CENTER OF EXPERTISE
12565 WEST CENTER ROAD
OMAHA, NEBRASKA 68144-3869

COPY

REPLY TO
ATTENTION OF:

February 8, 2002

Hazardous, Toxic and Radioactive Waste
Center of Expertise

General Engineering Laboratories, Inc.
ATTN: Robert Pullano
2040 Savage Road
Charleston, SC 29407

Gentlemen:

This correspondence addresses the recent evaluation of General Engineering Laboratories, Inc. of Charleston, SC, by the U.S. Army Corps of Engineers (USACE) for chemical analysis in support of the USACE Hazardous, Toxic and Radioactive Waste Program.

Your laboratory is now validated for the parameters listed below:

METHOD	PARAMETERS	MATRIX(1)
EPA 300	Anions(4)	Water(2)
9010B/9012A	Cyanide	Water(2)
9013/9014	Cyanide	Solids
8330	Explosives	Water(2)
8330	Explosives	Solids(2)
8151A	Herbicides	Water(2)
8151A	Herbicides	Solids
8081A	Organochlorine Pesticides	Water(2)
8081A	Organochlorine Pesticides	Solids
8082	Polychlorinated Biphenyls	Water(2)
8082	Polychlorinated Biphenyls	Solids(2)
8310	PAHs	Water(2)
8310	PAHs	Solids
8270C	Semivolatile Organics	Water(2)
8270C	Semivolatile Organics	Solids(2)
6010B/7000A	TAL Metals(3)	Water(2)
6010B/7000A	TAL Metals(3)	Solids(2)
9060	TOC	Water(2)
8015M	TPH-GRO/DRO	Water(5)
8015M	TPH-GRO/DRO	Solids(5)
8021B	Volatile Organics	Water(2)

committed to by your laboratory as a result of the Navy inspection will also apply to this USACE validation. The period of validation is 24 months and expires on February 8, 2004.

The USACE reserves the right to conduct additional laboratory inspection or to suspend validation status for any or all of the listed parameters if deemed necessary. It should be noted that your laboratory may not subcontract USACE analytical work to any other laboratory location without the approval of this office. This laboratory validation does not guarantee the delivery of any analytical samples from a USACE Contracting Officer Representative.

Any questions of comments can be directed to Richard Kissinger at (402) 697-2569. General questions regarding laboratory validation may be directed to the Laboratory Validation Coordinator at (402) 697-2574.

Sincerely,

for Marcia C. Davies, Ph.D.
Director, USACE Hazardous,
Toxic and Radioactive Waste
Center of Expertise

DEPARTMENT OF THE ARMY
CORPS OF ENGINEERS
HTRW CENTER OF EXPERTISE
12565 WEST CENTER ROAD
OMAHA, NEBRASKA 68144-3869

REPLY TO
ATTENTION OF:

April 4, 2002

Hazardous, Toxic and Radioactive Waste
Center of Expertise

Paradigm Analytical Laboratories, Inc.
ATTN: Greg Dickinson
2627 Northchase Parkway S. E.
Wilmington, NC 28405

Gentlemen:

This correspondence addresses the recent evaluation of Paradigm Analytical Laboratories, Inc. of Wilmington, NC by the U.S. Army Corps of Engineers (USACE) Hazardous, Toxic, and Radioactive Waste Center of Expertise (HTRW CX) for performing dioxin and furan analyses. Specifically evaluated were the following parameters:

METHOD	PARAMETERS	MATRIX
1613B	Dioxins/Furans	Water
8290	Dioxins/Furans	Water
8290	Dioxins/Furans	Solids

Evaluation of your laboratory for the analytical capabilities was based on the documents you submitted, which include Laboratory's Quality Program Plan, Statement of Qualifications, SOPs for Methods 8290 and 1613B, and state certifications.

The expiration date of validation is April 4, 2004. It should be noted that this office reserves the right to suspend acceptance status at any time if technical performance is found to be deficient.

DEPARTMENT OF THE ARMY
U.S. ARMY CORPS OF ENGINEERS
12565 WEST CENTER ROAD
OMAHA NE 68144-3869

REPLY TO
ATTENTION OF

September 26, 2003

Hazardous, Toxic and Radioactive Waste
Center of Expertise

Mr. Ray Piccione
Ecology and Environment, Inc.
4493 Walden Avenue
Lancaster, NY 14086

Dear Mr. Piccione:

This correspondence addresses the ongoing validation status of Ecology and Environment, Inc. of Lancaster, New York for the U.S. Army Corps of Engineers (USACE) for chemical analysis in support of the USACE Hazardous, Toxic and Radioactive Waste Program.

Ecology and Environment, Inc. of Lancaster, New York is now validated for the parameters listed below:

METHOD	PARAMETERS	MATRIX[4]
300 series	Anions[2]	Water[3]
8021B	AVO	Water[3]
8021B	AVO	Solids
8330	Explosives	Water
8330	Explosives	Solids
8021B	HVO	Water[3]
8021B	HVO	Solids
8270C	Semivolatile Organics	Water[3]
8270C	Semivolatile Organics	Solid[3]
9010B/9012A	Cyanide	Water[3]
9013/9012A	Cyanide	Solids
8151A	Chlorinated Herbicides	Water[3]
8151A	Chlorinated Herbicides	Solids
6010B/7000A	TAL Metals[1]	Water[3]
6010B/7000A	TAL Metals[1]	Solid[3]
6020A	TAL Metals[1]	Water[3,5]
6020A	TAL Metals[1]	Solid[3,5]
413.1	Oil & Grease	Water[3]
8081A	Pesticides	Water[3]
8081A	Pesticides	Solids[3]
8082	Polychlorinated Biphenyls	Water[3]

Printed on Recycled Paper

METHOD	PARAMETERS	MATRIX[4]
8082	Polychlorinated Biphenyls	Solids[3]
8310	Polynuclear Aromatic Hydrocarbons	Water[3]
8310	Polynuclear Aromatic Hydrocarbons	Solids[3]
9060	Total Organic Carbon	Water[3]
9060M	Total Organic Carbon	Solids
Mod 8015	TPH - DRO/GRO	Water[5]
Mod 8015	TPH - DRO/GRO	Solids[5]
418.1	TRPH	Water[5]
9071A/418.1	TRPH	Solids[5]
8260B	Volatile Organics	Water[3]
8260B	Volatile Organics	Solids[3]

Remarks:

(1) TAL Metals: Aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, nickel, potassium, selenium, silver, sodium, thallium, vanadium, and zinc.

(2) Anions: Chloride, fluoride, sulfate, nitrate, nitrite, and ortho-phosphate.

(3) The laboratory has successfully analyzed a proficiency testing sample for this method/matrix.

(4) 'Solids' includes soils, sediments, and solid waste.

(5) Approval for this parameter is based on review of SOPs only.

Based on the successful analysis of the National Environmental Laboratory Accreditation Conference Proficiency Testing samples for the appropriate fields of testing, the results of the laboratory inspection, and your Corrective Action Report, your laboratory will be validated for sample analysis by the methods listed above. The evaluation, which was conducted for your facility, is based substantially on ISO Guide 25 (General Requirements for the Competence of Testing Laboratories) and USACE Engineering Manual (EM) 200-1-3, Appendix I (Shell for Analytical Chemistry Requirements). The period of validation has been previously established and expires on January 3, 2005.

The USACE reserves the right to conduct additional laboratory inspections or to suspend validation status for any or all of the listed parameters if deemed necessary. It should be noted that your laboratory may not subcontract USACE analytical work to any other laboratory location without the approval of this office. This laboratory validation does not guarantee the delivery of any analytical samples from a USACE Contracting Officer Representative.

Any questions or comments can be directed to Dr. Richard Meyer at (402) 697- 2571. General questions regarding laboratory validation may be directed to the Laboratory Validation Coordinator at (402) 697-2574.

Sincerely,

for Marcia C. Davies, Ph.D.
Director, USACE Hazardous,
Toxic and Radioactive Waste
Center of Expertise

DEPARTMENT OF THE ARMY
CORPS OF ENGINEERS
HTRW CENTER OF EXPERTISE
12565 WEST CENTER ROAD
OMAHA, NEBRASKA 68144-3869

REPLY TO
ATTENTION OF:

January 13, 2003

Hazardous, Toxic and Radioactive Waste
Center of Expertise

GPL Laboratories, LLLP
ATTN: Elsa Tai
202 Perry Parkway
Gaithersburg, Maryland 20877

This correspondence addresses the recent evaluation of GPL Laboratories, LLLP of Gaithersburg, Maryland by the U.S. Army Corps of Engineers (USACE) for chemical analysis in support of the USACE Hazardous, Toxic and Radioactive Waste Program.

Your laboratory is now validated for the parameters listed below:

METHOD	PARAMETERS	MATRIX(1)
300 series	Anions(4)	Water(2)
8021B	Aromatic Volatile Organics	Water(2)
8021B	Aromatic Volatile Organics	Solids(2
9010B/9012A	Cyanide	Water(2)
9013/9012A	Cyanide	Solids(2
8330	Explosives	Water(2)
8330	Explosives	Solids(2)
8151A	Herbicides	Water(2)
8151A	Herbicides	Solids(2
7196A	Hexavalent Chromium	Water(2)
3060A/7196A	Hexavalent Chromium	Solids(2
413.1	Oil & Grease	Water(2)
8081A	Organochlorine Pesticides	Water(2)
8081A	Organochlorine Pesticides	Solids(2
314.0	Perchlorate	Water(2)
314.0M	Perchlorate	Solids(2
9065/9066	Phenolics	Water(2)
8082	Polychlorinated Biphenyls	Water(2)
8082	Polychlorinated Biphenyls	Solids(2)

Any questions or comments can be directed to Mr. Stephen Schnitker at (402) 444-4319. General questions regarding laboratory validation may be directed to the Laboratory Validation Coordinator at (402) 697-2574.

Sincerely,

Marcia C. Davies, Ph.D.
Director, USACE Hazardous,
Toxic and Radioactive Waste
Center of Expertise

Enclosure

DEPARTMENT OF THE ARMY
CORPS OF ENGINEERS
HTRW CENTER OF EXPERTISE
12565 WEST CENTER ROAD
OMAHA, NEBRASKA 68144-3869

REPLY TO
ATTENTION OF:

RECEIVED
JAN 03 2003
By SAC

December 23, 2002

Hazardous, Toxic and Radioactive Waste
Center of Expertise

Pace Analytical Services, Inc.
ATTN: Sarah Cherney
1700 Elm Street, Suite 200
Minneapolis, MN 55414

Gentlemen:

This correspondence addresses the ongoing validation status of Pace Analytical Services, Inc., Minneapolis, MN for the U.S. Army Corps of Engineers (USACE) for chemical analysis in support of the USACE Hazardous, Toxic and Radioactive Waste Program.

Pace Analytical Services, Inc., Minneapolis, MN is now validated for the parameters listed below:

METHOD	PARAMETERS	MATRIX(1)
8290	Dioxins/Fur-N	Water
8290	Dioxins/Fur-N	Solids(2)
TO-3	Volatile Organics	Air(3)
TO-14A/15	Volatile Organics	Air(3)

Remarks:

1) 'Solids' includes soils, sediments, and solid waste.

2) The laboratory has successfully analyzed a Proficiency Testing (PT) sample for this method/matrix.

3) Compendium Method TO-14A/TO-15 using evacuated canister and GC/MS analysis

Based on the successful analysis of the National Environmental Laboratory Accreditation Conference Proficiency Testing samples for the appropriate fields of testing and the submission of acceptable SOPs and supporting documentation, your laboratory will be validated for sample analysis by the methods listed above. The evaluation, which was conducted for your facility, is based substantially on ISO Guide 25 (General Requirements for the Competence of Testing

Laboratories) and USACE Engineering Manual (EM) 200-1-3, Appendix I (Shell for Analytical Chemistry Requirements). The period of validation for all parameters has been previously established and expires on November 19, 2004.

The USACE reserves the right to conduct additional laboratory inspections or to suspend validation status for any or all of the listed parameters if deemed necessary. It should be noted that your laboratory may not subcontract USACE analytical work to any other laboratory location without the approval of this office. This laboratory validation does not guarantee the delivery of any analytical samples from a USACE Contracting Officer Representative.

Any questions or comments can be directed to Jim Cheney at (402) 697-2565. General questions regarding laboratory validation may be directed to the Laboratory Validation Coordinator at (402) 697-2574.

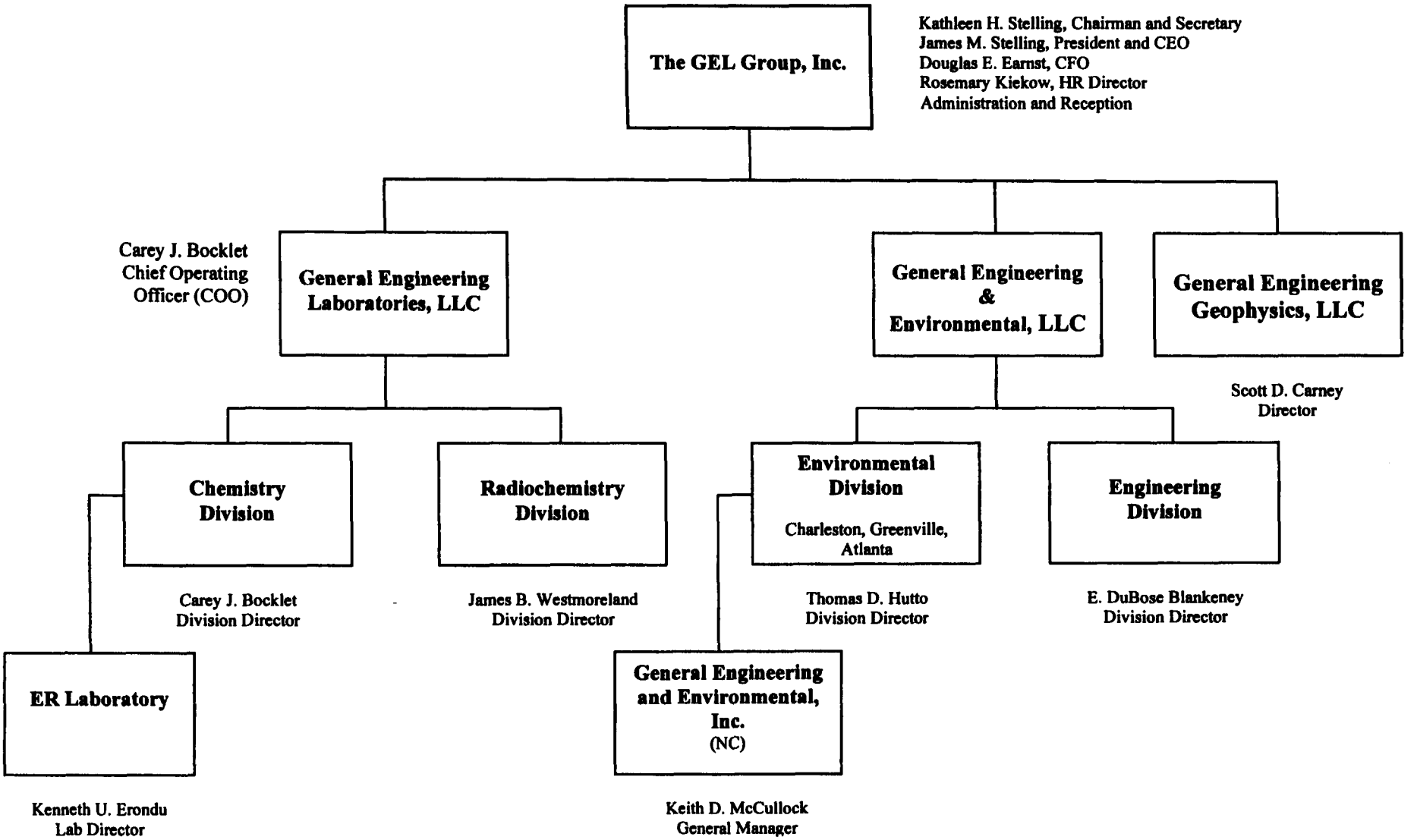
Sincerely,

for Marcia C. Davies, Ph.D.
Director, USACE Hazardous,
Toxic and Radioactive Waste
Center of Expertise

Appendix B

APPENDIX B
Laboratory Organizational Charts

The GEL Group, Inc.
Organization Chart February 2003



General Engineering Laboratories, LLC
Client and Support Services

Client and Support Services

Richard Detar

Contracts and Proposals

Tasha Horton
Anna White
Alyssa Wingard

Federal Project Management

Angela Brown
Valerie Davis
Patricia Dover
Dionne Francis
Cheryl Jones
Edie Kent
Sarah Kozlik
Wendi Lane
David Setzer
Laura Sluss
Julie Strock
Open

Industrial Project Management

Jake Crook
Amy Jamison
Tom Seabrook
Amy Neidfelt

Couriers

Tom Carter (pt)
Bob Lockhart

Sample Receiving Bottle Prep Waste

Pete Wilber*
William Covington
Mike Kinslow
Elijah Singleton
Mellie Smith
Mary Stoner
Nick Osborn
Scott Mostoller
Open

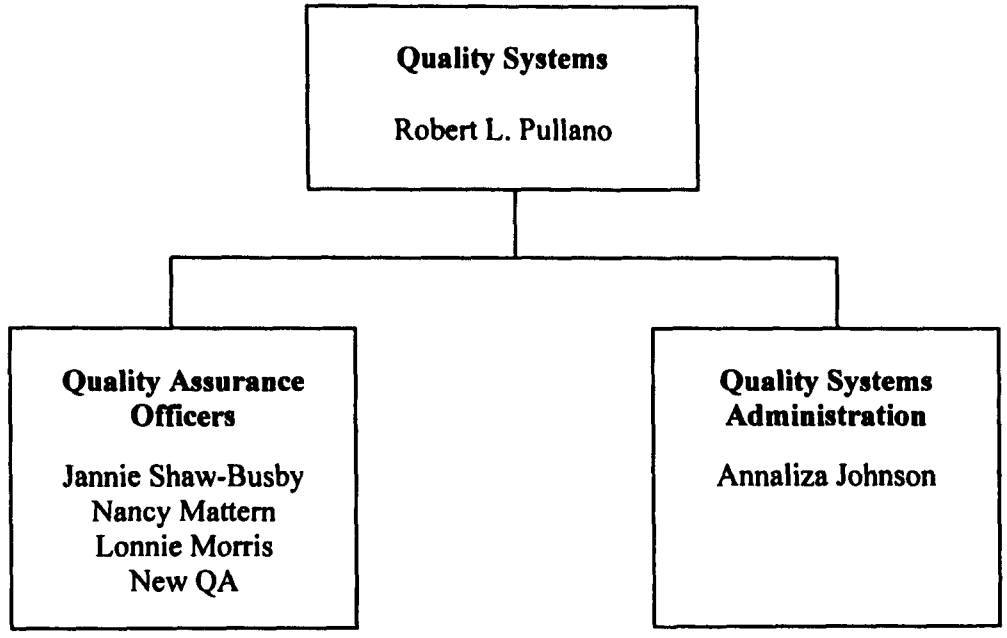
Purchasing

Ben Munford

*Group Leader

October 2003

General Engineering Laboratories, LLC
Quality Systems



October 2003

General Engineering Laboratories, LLC
Chemistry Laboratory

Chemistry Laboratory
Carey J. Bocklet

Technical Development
Linda Darrington
Jeff Denton

Production Manager
Pat Steele

General Chemistry
Joey Boyd*
Brian Burgess
Jennifer Dunagan
Amy Fournier
Julia Hamilton
Martha Harrison
Virginia Hoffman
Tom Lewis
Theresa McKelvey
James Maestas
Erin Norton
Deidre Reilly
Shannon Schalles
Mary Sherwood
Louise Smith
Ella Szulc
Paulette Wendell

Metals
Jamie Johnson*
Frankie Armstrong
Brandon Bottomley
Paul Boyd
Helen Camello
Bryan Davis
Allison Evans
April Grant
Joanne Harley
Cedric High
Elizabeth Janssen
Rose Jenkins
Eric Lawson
Emily Martin
Nik-Cole Robinson
Barbara Seigler

Cameron Bearden*

Semivolatiles
Kelle Bellamy
Richard Bomar
Lloyd Fox
Johnnie Frazier
Erin Haubert
Chris Kerr
Herb Maier
Jason Pierce
Alberto Rodriguez
Janice Willey
Mike Penny

Pesticides/PCBs
Josh Brooks
Jimin Cao
Gwen Hallquist
Sharlene Jackson
Jason Pierce
Yiping Shi
Jared Wagner
Brian Parsons

Volatiles
Joey Amundsen *
Johnny Bell
Linda Dashnaw
Sara Jones
Debbie Smith
Crystal Stacey
Anson Walsh
Charles Wilson
Tammy Woodie

Organic Prep
Joey Amundsen*
Gelester Baskett
Erin Dobson
Harris Frampton
Nathaiel Long
Jo Patrick
Maria Simons
Kahle Van Staveren
Nathan Greene
Clarice White

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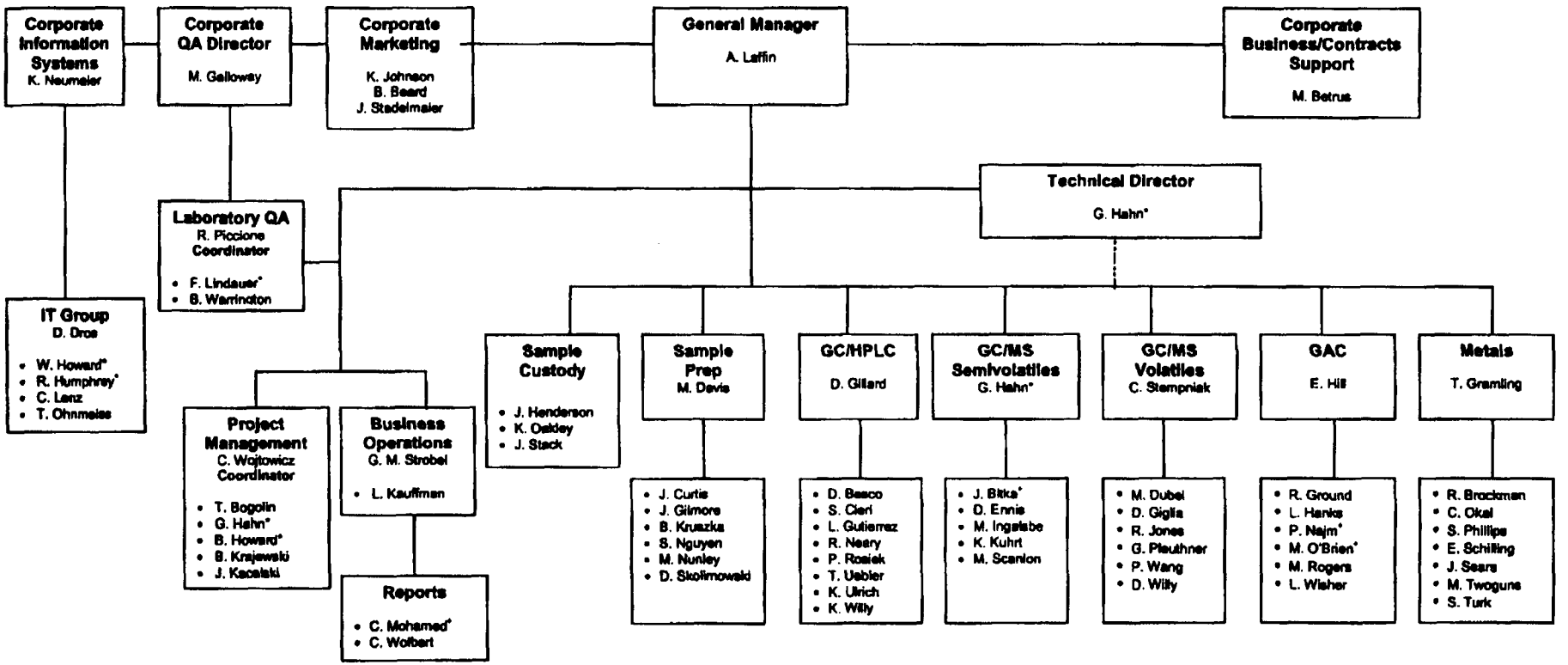
Vonda Fields*
Candy Bell
Sherri Brown
Vonda Fields
LySandra Gathers
Joan Gaillard
Rommel Gomez
Flora Ingram
Yvette Lampkin
Linda Pullano (pt)
Traci Widener
Amy Niedfeldt
Kalisha Johnson

* Group Leader

February 2004



* Dual Assignment
** On-Call
\+ Part Time

-···-Technical Supervision of Operations

Ecology & Environment
ASC ORGANIZATIONAL PLAN

L:\Marketing\proposal_boilerplate\F105 Org Chart.doc\Rev. 0/Approval Date: 4/3/01/Last Update: 05/03/04

Paradigm

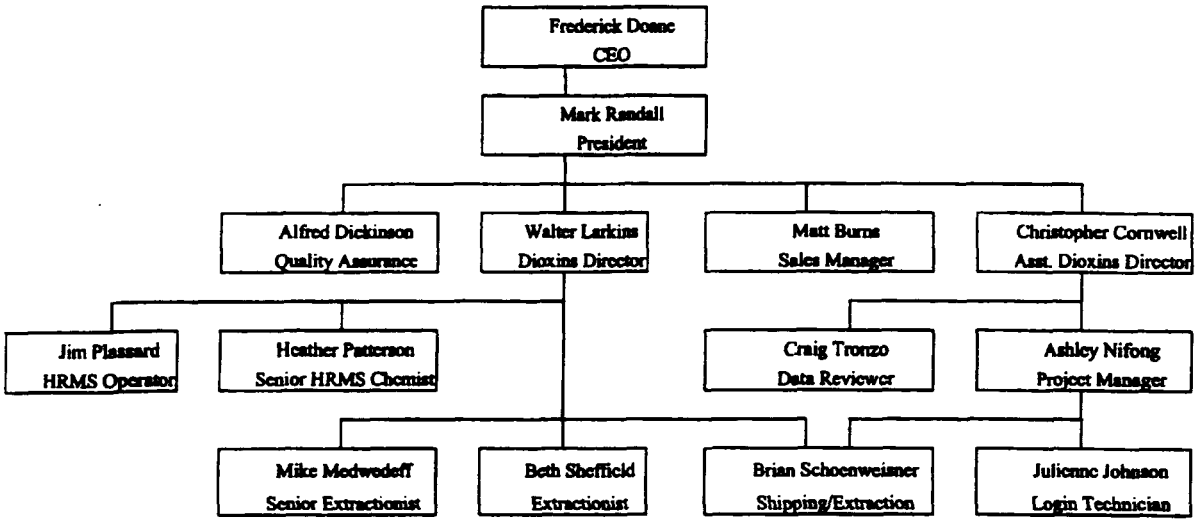
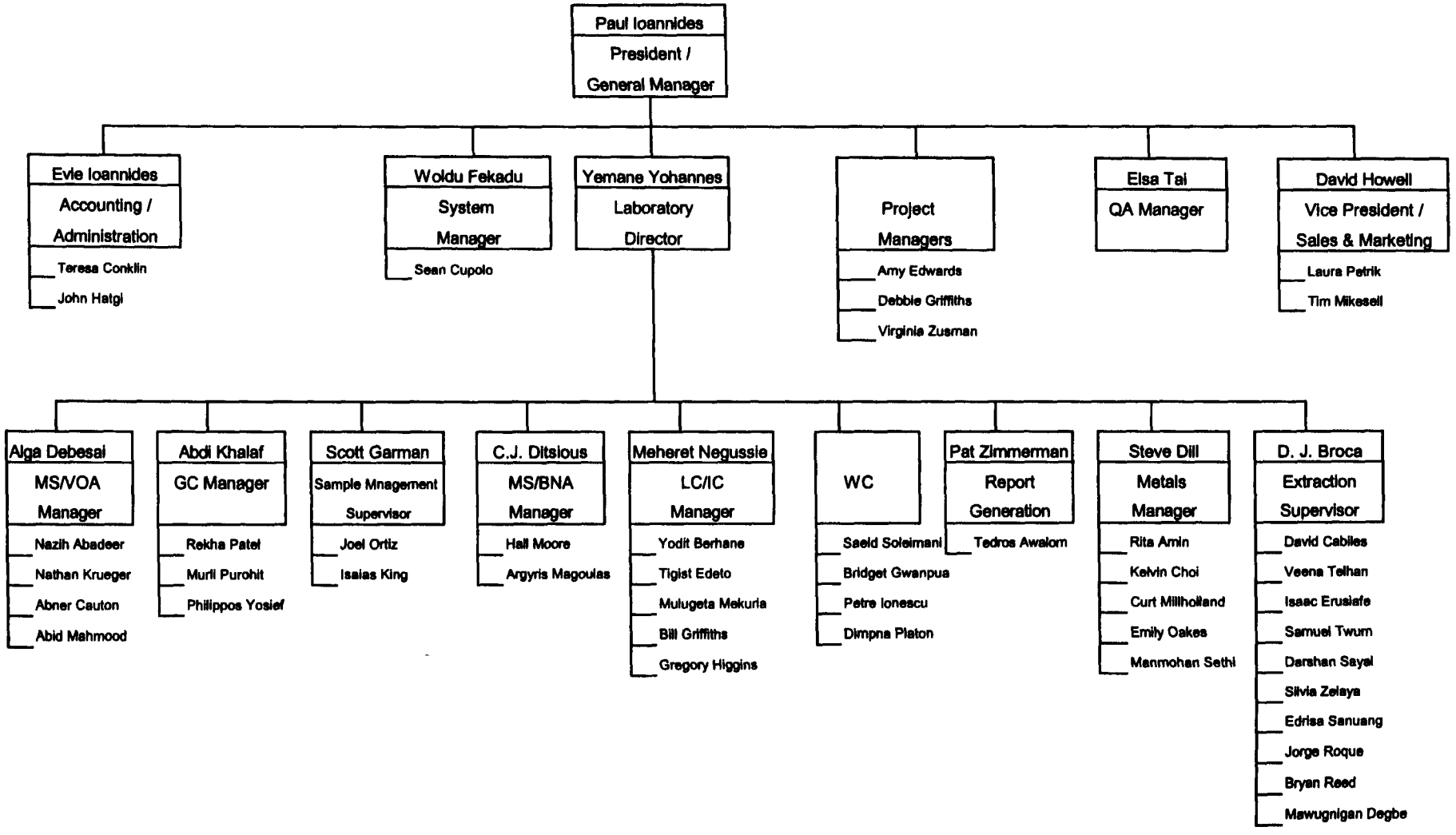


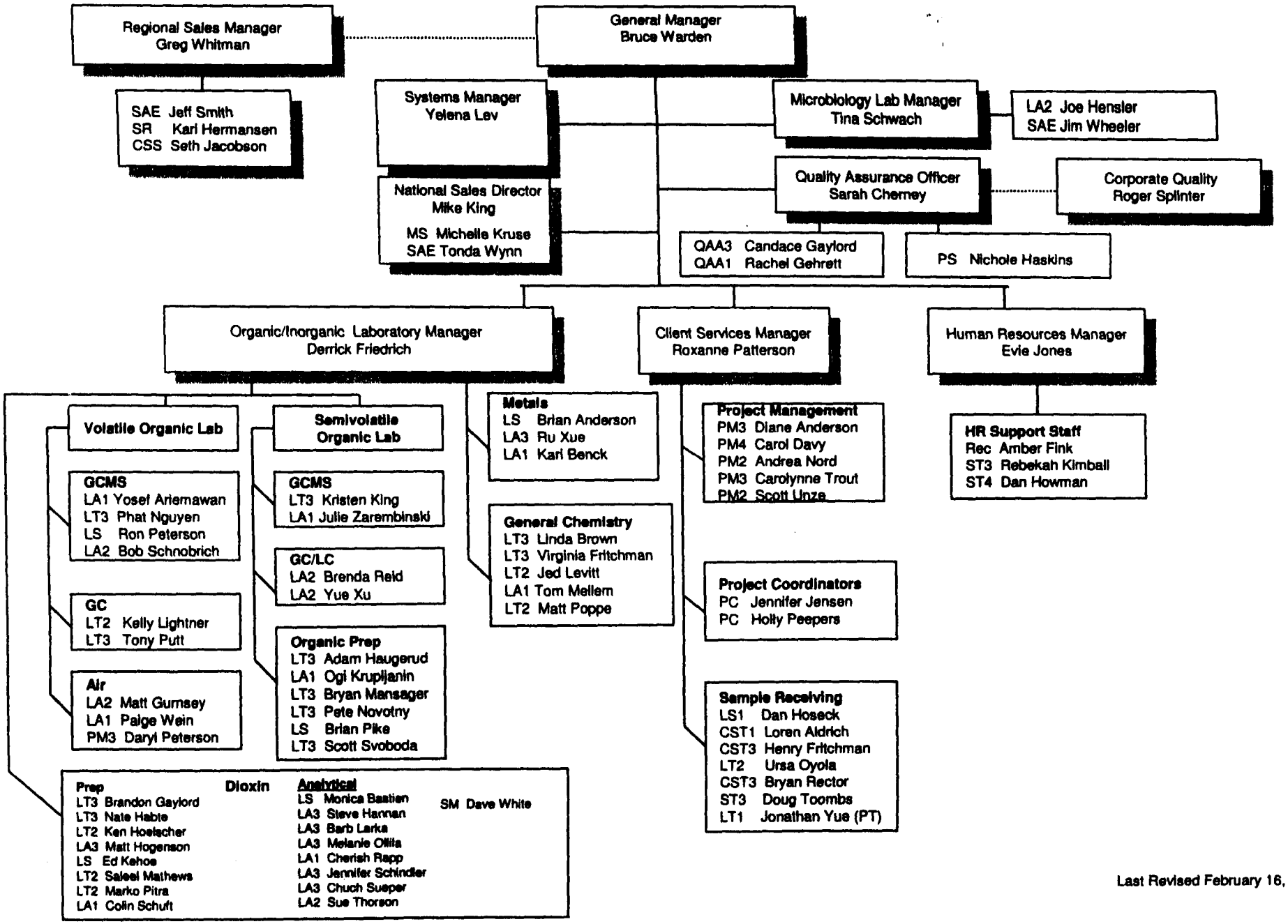
Figure 1. Organizational Chart

February-2004

GPL Laboratories Organizational Chart



MN Lab



Last Revised February 16, 2004

Appendix C

APPENDIX C
Laboratory SOPs

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

CLOSED-SYSTEM PURGE-AND-TRAP

COLLECTION AND EXTRACTION

VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

APPLICABLE TO METHOD:
EPA SW-846 Method 5035

(GL-OA-E-039 REVISION 5)

PROPRIETARY INFORMATION

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GEL's Document Control Officer certifies this document to be a true copy of the fully executed original.

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4.0 METHOD APPLICABILITY AND METHOD SUMMARY 3
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1.0 CLOSED-SYSTEM PURGE-AND-TRAP COLLECTION AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

2.0 METHOD CODE

EPA SW-846 Methods 5035

3.0 METHOD OBJECTIVE AND PURPOSE

3.1 This procedure can be used to quantify most volatile organic compounds that have:

3.1.1 A boiling point below 200°C

3.1.2 Are insoluble or slightly soluble in water.

3.2 This method is applicable for use with GL-OA-E-038 (SW846 Method 8260B) "Volatile Organic Compounds by GC/MS."

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in 5030B. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

4.2 The low soil method utilizes a hermetically sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are negligible. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 1.0 to 100 µg/kg range

4.3 Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

4.4 Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent. These samples are also purged using Method 5030.

4.5 Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique. However, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency.

4.6 The closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030.

5.0 METHODS SCOPE AND PERFORMANCE CHARACTERISTICS

5.1 Low concentration soil method - generally applicable to soils and other solid samples with VOC concentrations in the range of 1.0 to 100 µg/kg. Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a

septum-sealed screw cap that already contains a stirring bar and either a sodium bisulfate preservative solution or organic free DI water. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

5.2 High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 100 µg/kg. The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 100 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS). Collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw cap (see Sec 4) that contains 10 mL of a water-miscible organic solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

5.3 Method Detection Limit and Practical Quantitation Limit (PQL):

5.3.1 The practical quantitation limits can be as low as 1.0 µg/L for most compounds. Compounds will have the same PQL as the lowest multipoint level for that compound. Please see the analytical methods identified in section 3.2.

5.3.2 Method detection limit studies are performed annually and are kept in the volatile section.

6.0 REFERENCES

6.1 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1(Part 2) Section B. SW-846, Third Edition. Method 8260B, "Volatile Organic Compounds by Gas Chromatograph/Mass Spectrometer (GC/MS): Capillary Column Technique," Revision 1, September 1994. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

6.2 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1(Part 2) Section B. SW-846, Third Edition. Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," Revision 0, December 1996. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460

7.0 INTERFERENCES TO THE METHOD

7.1 Potential contaminants for this procedure include common laboratory solvents, typically ketones, methylene chloride, toluene, and freon.

7.2 To minimize the contamination, use organic-free deionized water or equivalent for all analyses.

7.3 Contamination by carry-over can occur during sequential analyses. If carry-over is suspected, the affected sample or samples are reanalyzed.

7.4 The trap and other parts of the system, such as the column, are subject to contamination; therefore frequent bake out and purging of the system is required. For more detail on this subject, see the method.

8.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

8.1 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client MSDS forms are also maintained.

8.2 Personal protective equipment

8.2.1 Approved gloves are required when handling compounds and samples in this procedure.

8.2.2 Work under a hood when using concentrated acids, bases, and stock solutions.

8.3 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling.

8.4 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.5 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

8.6 In the event of an accident or medical emergency, seek help immediately. When time and safety permit, file an accident report form regardless of how insignificant the injury may seem.

8.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

9.0 CAUTION WARNINGS

The analyst must use great care when operating and assembling instrumentation and when handling samples and reagents. Check to see that the equipment is properly assembled and connected to gas and power, etc. Take great care to avoid running samples that contain overrange hits of analytes, especially hydrocarbons. Samples are stored without headspace at either 4° ±2°C or -10°C to -20°C (if preserved in organic free DI water), and are not stored with standards. Sample dilutions will only be made with organic-free, DI water or equivalent.

10.0 APPARATUS AND MATERIALS, REAGENTS, EQUIPMENT AND INSTRUMENTS

10.1 Ancillary Equipment

10.1.1 25 mL or 10 mL glass syringes - manufactured by Hamilton (ordered from Baxter)

10.1.2 Gas tight syringes - 1 µL, 10 µL, 25 µL, 50 µL, 100 µL, 1000 µL (ordered from Baxter)

10.1.3 Purge vessels - Hammett Glassware, Dynatech or Tekmar

10.1.4 Volumetric flasks

10.1.5 Drying oven

10.1.6 Refrigerator

10.1.7 Freezer

10.1.8 40 mL glass vials

10.1.9 Reactor vials

10.1.10 Centrifuge

10.1.11 Disposable pipettes

10.1.12 Top-loading balance - Capable of accurately weighing to 0.01 g

10.1.13 18mm x 150mm Culture tubes

10.1.14 Magnetic stirring bars- PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars.

10.2 Field Sampling Equipment

10.2.1 Purge-and-Trap Soil Sampler - Model 3780PT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

10.2.2 EnCore sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), TM or equivalent.

10.2.3 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

10.2.4 Portable balance - For field use, capable of weighing to 0.01 g.

10.2.5 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, reagent water added, cap, and septum.

10.3 Reagents

10.3.1 Water used for any analysis should be organic-free DI water or equivalent. Store bought distilled water can be used in some instances if it is screened before use.

10.3.2 Methanol: B and J brand (or equivalent) high purity solvent for purge and trap analysis. Each batch of methanol is screened for contaminants prior to use.

10.3.3 Source, Working, Surrogate, and Internal Standard Solutions: Most standard solutions are purchased from approved vendors. Standards are used to make stock, intermediate, and working standards (refer to the referenced analytical SOP's given in Section 3.2).

10.3.4 Methanol is screened by "lot" for contaminants prior to use.

10.3.5 Low concentration sample preservative

10.3.5.1 Sodium bisulfate, NaHSO - ACS reagent grade or equivalent.

10.3.5.2 Water – DI water or equivalent

10.3.5.3 The preservative should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

10.3.5.4 If preserved in water the sample must be frozen within 48 hours of sampling.

10.4 Instrumentation

10.4.1 A Closed System Purge and Trap. This instrument consists of a unit that automatically adds water, surrogates, and internal standards to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph.

10.4.1.1 The purging device is designed to accept a vial sufficiently large enough to contain a 5-gm soil sample plus a magnetic stirring bar and 10 mL of water

10.4.1.2 The concentrator consists of a Vocarb (or equivalent) trap that is 25 cm long, and has an inside diameter of 0.105 inches.

10.4.1.3 The packing material is Carbopack B/Carboxen (or equivalent).

10.4.1.4 The heater assembly is used to maintain samples at 40°C.

10.4.2. Purge and Trap system for water and high level soil and waste samples is described in GL-OE-E-038. This system consists of three parts, an autosampler, concentrator, and heater assembly. The specifications can be found in the analytical procedures.

10.4.3 See the appropriate analytical procedure (identified in Section 3.2) for instrument set up and specifications and conditions.

11.0 SAMPLE COLLECTION HANDLING AND PRESERVATION REQUIREMENTS

11.1 Refer to the introductory material in Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1(Part 2) Section B. SW-846, Third Edition Organic Analytes, Sec. 4.1, for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

11.2 Preparation of sample vials

11.2.1 Low concentration soil samples.

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035. All vials received at GEL are from an approved vendor containing the stir bar, preservative and water and have with them a certificate of cleanliness when received from the vendor.

11.2.1.1 Add a clean magnetic stirring bar to each clean vial.

11.2.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of <2. If the samples are known or suspected to contain high levels of carbonates, do not add preservative, and skip to step 11.2.1.3.

11.2.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution. Samples without preservative need to be frozen within 48 hours of collection. The

acid solution or freezing will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

11.2.1.4 Seal the vial with the screw cap and septum seal.

11.2.1.5 Affix a label to each vial.

11.2.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

11.2.2 High concentration soil samples

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in SW846 Method 5030(See section 3.2 for appropriate analytical procedure). Vials are purchased by GEL from an approved vendor containing methanol along with certification, or follow steps 11.2.2.1 through 11.2.2.5.

11.2.2.1 Add 10 mL of methanol to each vial.

11.2.2.2 Seal the vial with the screw cap and septum seal.

11.2.2.3 Mark the meniscus of the solvent on the side of the vial. This will identify if any evaporation has taken place between vial preparation and sample collection. Vials should be discarded if any evaporation has been identified.

11.2.2.4 Affix a label to each vial.

11.2.2.5 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

11.2.3 Oily waste samples

When oily waste samples are known to be soluble in methanol, sample vials may be prepared as described in 11.2.2, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in 11.2.2.

11.3 Field sample collection (if samples are not transferred to VOA vials in field, see section 12.2)

Collect the sample according to the procedures outlined in the sampling plan. 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 the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the EnCore sampler, the Purge-and-Trap Soil Sampler, and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

11.3.1 Collection of Low concentration soil samples

11.3.1.1 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

11.3.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw cap. Store samples on ice at 4°C. 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 collect low concentration samples in vials that do not contain the preservative solution.

11.3.1.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed. Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

11.3.1.4 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

11.3.1.5 As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for reanalysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

11.3.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, and dry weight determination in a container that does not have preservation solution.

11.3.17 If high concentration samples are collected in vials containing methanol, then two additional aliquots should be collected, one for high concentration analysis collected in a vial containing methanol, and another for the dry weight determination, as described in 11.3.1.6.

11.3.1.8 The EnCore ™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore ™ device may be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, or analyzed within 48 hours.

11.3.2 Collection of High concentration soil samples

11.3.2.1 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

11.3.2.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the vial containing 10 mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw cap. Store samples on ice at 4°C.

11.3.2.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed. Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

11.3.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

11.3.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

11.3.2.7 The collection of at least one additional sample aliquot is required for the determination of the dry weight.

11.3.3 Collection of Oily waste samples

11.3.3.1 When an oily waste is known to be soluble in methanol, the sample may be collected in a vial containing such a solvent using procedures similar to those described in Sec. 11.2.2

11.3.3.2 When the solubility of the oily waste is not known, the sample should either be collected in a vial without a preservative, as described in 11.2.2, or the solubility of a trial sample should be tested in the field, using a vial containing solvent. If the trial sample is soluble in the solvent, then collect the oily waste sample as described in 11.2.2. Otherwise, collect an unpreserved sample.

12.0 SAMPLE HANDLING, SHIPMENT AND STORAGE

12.1 Sample shipment

12.1.1 All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan.

12.2 Sample preparation

12.2.1 Verify all sample descriptions match laboratory sample ID numbers.

12.2.2 For samples received in EnCore™ sampling devices (or similar):

12.2.2.1 Check the sample for effervescence:

12.2.2.1.1 Take small amount of sample from the container used for moisture measurement and add to a disposable cup.

12.2.2.1.2 Add a few milliliters of sodium bisulfate preservation solution and observe for reaction.

NOTE: if samples effervesce, add 5 milliliters of organic free water to a 40-ml vial that contains a stir bar;

tare the vial; add sample from EnCore™ of other sampling device as described below and freeze.

12.2.2.1.3 The laboratory routinely preserves Encore sample in water with subsequent freezing. Holding time for Encore preservation is 48 hours from collection. Frozen sample holding time is 14 days from collection. The laboratory must allow the frozen sample to thaw prior to analysis. Upon thawing the sample must be analyzed within 24 hours. Unless otherwise required by the client, preservation by freezing is used on all 5035 low level soils preserved in the laboratory.

12.2.2.1.4 Encore preservation dates and times are recorded in the sample preparation logbook adjacent to the hood in the volatile organics laboratory. The date and time of preservation is also indicated in the "sample Prep" entry in the laboratory LIMS system. This date and time will always indicate the date and time that the sample was preserved or prepped for analysis, either by the lab or field crews. If the samples were preserved in the field, the date and time of the sample prep in LIMS will also match the date and time of collection.

12.2.2.2 Preserving the sample:

12.2.2.2.1 Place vial that contains preservative onto the balance.

12.2.2.2.2 Tare the balance.

12.2.2.2.3 Remove vial from balance and remove the cap.

12.2.2.2.4 Quickly open the cover of the sampling device.

12.2.2.2.5 Quickly add total content of the sampling device into the vial.

12.2.2.2.6 Quickly close the vial.

12.2.2.2.7 Weigh the vial.

12.2.2.2.8 Record weight.

12.2.2.2.9 Record the preservative.

12.2.2.2.10 Record the lot# of vial preservative kit.

12.2.3 For samples received preserved from the field:

12.2.3.1 Tare the balance.

12.2.3.2 Place vial onto the balance and record weight.

12.2.3.3 Record the initial weight of the tared vial.

12.2.3.4 Record the preservative.

12.2.3.5 Record the lot# of vial preservative kit.

12.2.4 For samples not preserved in the field and not received in EnCore™ sample device:

NOTE: Clients are notified if containers do not meet method specifications prior to sample login. Assume that the client has been notified of the situation and has given approval for continued processing of the sample.

12.2.4.1 Place vial that contains preservative onto the balance.

12.2.4.2 Tare the balance.

12.2.4.3 Remove vial from balance and remove the cap.

12.2.4.4 Quickly open the cover of the sample container.

12.2.4.5 Quickly add 5±1.0 grams of sample into the vial.

12.2.4.6 Quickly close the vial.

12.2.4.7 Weigh the vial.

12.2.4.8 Record weight.

12.2.4.9 Record the preservative.

12.2.4.10 Record the lot# of vial preservative kit.

12.2.4.11 Narrate which container was used for sample preservation in the comment section of the logbook.

12.3 Sample storage

12.3.1 Once in the laboratory, store samples at either 4°C (preserved) or -10°C (unpreserved) until analysis. The sample storage area should be free of organic solvent vapors.

12.3.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

12.3.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, storage of low concentration samples at -10°C (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel.

13.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

13.1 Routine Preventative and Special Operational (Failure)

13.1.1 Autosampler maintenance is very sample dependent. In general, easy maintenance consists of changing the trap and line cleaning. Line cleaning is accomplished by back flushing the system with methanol.

13.1.2 If a glass jet separator is used, the frequency of maintenance for this device is sample dependent. This is a very detailed and delicate maintenance procedure and extreme care must be taken when cleaning.

13.2 Routine Preventative Maintenance (PM) Procedures

Preventive maintenance consists mainly of baking the trap following the analysis of samples.

13.3 Non-routine Maintenance Procedures (Special, Operational or Failure Mode Maintenance)

Troubleshooting the autosampler and instrument is a function of analyst experience. There are literally dozens, if not hundreds, of possible reasons for why the instruments do not operate efficiently and properly. In-house service is obtained from the Service Technician. If vendor assistance is needed, then the appropriate vendor is contacted.

13.4 Maintenance logbooks are kept for each instrument and include entries for both routine as well as non-routine maintenance procedures.

14.0 PREPARATION OF STANDARD SOLUTION AND QUALITY CONTROL SAMPLES

See the appropriate analytical procedure identified in Section 3.2 for preparation of standard solutions.

15.0 INSTRUMENT CALIBRATION AND PERFORMANCE REQUIREMENTS

Please see the instrument calibration information in the appropriate referenced method identified in Section 3.2.

16.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

Please see the analyst and method verification requirements information in the appropriate analytical method from Section 3. 2.

17.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

Please see the analysis procedures and instrumental operation information in the appropriate analytical method from Section 3.2.

18.0 CALCULATIONS AND DATA REDUCTION METHODS

Please see the calculations and data reduction methods information in the appropriate analytical method from Section 3.2.

19.0 DATA RECORDING

Please see the data recording information in the appropriate analytical method from Section 3.2.

20.0 QUALITY CONTROL REQUIREMENTS

Please see the quality control requirements information in the appropriate analytical method from Section 3.2.

21.0 DATA REVIEW, VALIDATION AND APPROVAL PROCEDURES

Please see the data review, validation and approval procedures information in the appropriate analytical method from Section 3.2.

22.0 DATA TRANSMITTAL

Please see the data transmittal information in the appropriate analytical method from Section 3.2.

23.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

24.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE
FOR
VOLATILE ORGANIC COMPOUNDS (VOC)
BY
GAS CHROMATOGRAPH/MASS SPECTROMETER

(GL-OA-E-038 REVISION 8)

APPLICABLE TO METHODS:

EPA SW-846 Method 8260A
EPA SW-846 Method 8260B
EPA SW-846 Method 5030A
EPA SW-846 Method 5030B
EPA SW-846 Method 5035

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1.0 STANDARD OPERATING PROCEDURE FOR VOLATILE ORGANIC COMPOUNDS (VOC) BY GAS CHROMATOGRAPH/MASS SPECTROMETER

2.0 METHOD CODE:

EPA SW-846 Methods: 8260A, 8260B, 5030A, 5030B, and 5035

3.0 METHOD OBJECTIVE AND PURPOSE

3.1 This procedure covers the determination of purgeable organic compounds in a variety of solid and liquid waste matrices. The volatile organic compounds are purged and absorbed onto a trap, separated via the gas chromatograph (GC), and detected using a mass spectrometer. This procedure can be used to quantify most volatile organic compounds that have:

3.1.1 A boiling point below 200°C

3.1.2 Are insoluble or slightly soluble in water.

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 Analytes - See Appendix 1.

4.2 Applicable Matrices - Groundwater, aqueous sludges, caustic liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filtercakes, spent carbons, spent catalysts, soils, wastewaters, and sediments.

4.3 General Method Summary - EPA Method 8260A/B is used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. The volatile compounds are introduced into the gas chromatograph via a purge and trap system using EPA SW-846 Methods 5030A for soils and waters under 8260A; 5030B for water and high level soils under 8260B; and SW-846 Method 5035 for low level soils under 8260B.

5.0 METHOD SCOPE AND PERFORMANCE CHARACTERISTICS

5.1 Calibration Range can be as low as 0.5 ppb up to 100 ppb for most analytes. The range for those analytes with poorer purging efficiencies can be as low as 5.0 ppb up to 5000 ppb.

5.2 Tested Concentration Range: The tested concentration will be the same as the calibration range, with no upper limit if dilutions are performed.

5.3 Method Detection Limit and Practical Quantitation Limit (PQL):

5.3.1 The practical quantitation limit for each analyte is the same as the analyte's lowest calibration concentration.

5.3.2 Method detection limit studies are performed annually and maintained as quality records.

5.3.3 Method detection limits are verified on each instrument.

6.0 REFERENCES

6.1 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1(Part 2) Section B. SW-846, Third Edition. Method 8260B, "Volatile Organic Compounds by Gas Chromatograph/Mass Spectrometer (GC/MS): Capillary Column Technique," Revision 1, September 1994. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

6.2 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1(Part 2) Section B. SW-846, Third Edition. Method 8000B, "Determinative Chromatographic Separations," Revision 3, December 1996. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460

6.3 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1(Part 2) Section B. SW-846, 3rd Edition. Method 5030B, "Purge-and-Trap for Aqueous Samples," Revision 2, December 1996. USEPA Office Of Solid Waste and Emergency Response, Washington, DC 20460

6.4 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1(Part 2) Section B. SW-846, Third Edition. Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," Revision 0, December 1996. USEPA Office Of Solid Waste and Emergency Response, Washington, DC 20460

6.5 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1B. SW-846, 3rd Edition. Method 8260A, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometer (GC/MS): Capillary Column Technique", Revision 1, September 1994. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460

6.6 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1B, SW-846, 3rd Ed., Method 5030A, "Sample Preparation and Extraction for Analysis of Volatile Organics by Purge and Trap", Rev 1, July 1992. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460

7.0 INTERFERENCES TO THE METHOD

7.1 Potential contaminants for this procedure include common laboratory solvents, typically Ketones, Methylene chloride, Toluene, and Freon.

7.2 To minimize the contamination, use organic-free DI water or equivalent for all analyses.

7.3 Contamination by carry-over can occur during sequential analyses. If carry-over is suspected, the affected sample or samples are reanalyzed.

7.4 The trap and other parts of the system, such as the column, are subject to contamination; therefore frequent bake out and purging of the system is required.

8.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

8.2 Treat all chemicals as a potential health hazard and limit exposure to them to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals used in this SOP. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this SOP via GEL's Intranet. If necessary, contact the safety coordinator for specific MSDS sheets.

8.3 Personal protective equipment

8.3.1 Approved gloves are required when handling compounds and samples in this procedure.

8.3.2 Work under a hood when using concentrated acids, bases, and stock solutions.

8.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling.

8.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

8.7 In the event of an accident or medical emergency, seek help immediately. When time and safety permit, file an accident report form regardless of how insignificant the injury may seem.

8.8 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

9.0 CAUTION WARNINGS

The analyst must use great care when operating and assembling instrumentation and when handling samples and reagents. Check to see that the equipment is properly assembled and connected to gas and power, etc. Take great care to avoid running samples that contain over-range hits of analytes, especially hydrocarbons. Observe samples for foaming. Samples are stored without headspace at 4° ±2°C and are not stored with standards. Sample dilutions will only be made with organic-free, deionized water or equivalent.

10.0 APPARATUS AND MATERIALS; REAGENTS; EQUIPMENT AND INSTRUMENTS

10.1 Ancillary Equipment

10.1.1 25 mL or 10 mL glass syringes - manufactured by Hamilton
10.1.2 Gas tight syringes - 1 µL, 10 µL, 25 µL, 50 µL, 100 µL, 1000 µL
10.1.3 Purge vessels – 40 mL glass vials, Sparge Vessels
10.1.4 Volumetric flasks
10.1.5 Drying oven
10.1.6 Refrigerator and Freezer
10.1.7 Columns

10.1.7.1 J and W DB 624 fused silica capillary column 0.25mm ID x 60m, 1.4 µm film thickness

10.1.7.2 J and W DB 624 fused silica capillary column 0.25 mm ID x 30m, 1.4 µm film thickness

10.1.7.3 Restek RTX-Volatiles fused silica capillary column 0.25 mm ID x 30m, 1.0 µm film thickness

10.1.8 40 mL glass vials with open tops and septa
10.1.9 Reactor vials with mininert values
10.1.10 Centrifuge
10.1.11 Disposable pipets
10.1.12 Balance
10.1.13 18mm x 150mm Culture tubes

10.2 Reagents

10.2.1 Water used for volatile organic analysis must be high quality organic free water or equivalent.

10.2.2 Methanol: B and J brand high purity solvent for purge and trap analysis. Each lot of methanol is screened for contaminants prior to use.

10.2.3 Source Standard Solutions: Most source standard solutions are purchased from approved vendors. Source standards are used to make stock, intermediate, and working standards (refer to Section 14). The primary source standards used for calibrating the instrument are listed below. The title in bold face print is the common name of the solution.

10.2.3.1 <u>Federal Calibration Long List:</u>

Acetone	1,2-Dichloropropane
Acetonitrile	2,2-Dichloropropane
Benzene	1,3-Dichloropropane
Bromobenzene	cis-1,2-Dichloroethene

Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
4-Bromofluorobenzene
2-Butanone (MEK)
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Carbon Disulfide
Carbon tetrachloride
Chlorobenzene
Chloroethane
Chloroform
Chloromethane
Cyclohexane
2-Chloroethylvinyl ether
2-Chlorotoluene
4-Chlorotoluene
Dibromochloromethane
Dibromofluoromethane
Dichloromethane (Methylene chloride)
Dichlorodifluoromethane
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane (Ethylene dibromide)
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,1-Dichloropropene
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
Ethyl ether
Methyl acetate
cis-1,3-Dichloropropene
trans-1,2-Dichloroethene
trans-1,3-Dichloropropene
Ethylbenzene
Hexachlorobutadiene
2-Hexanone
Iodomethane
Isopropylbenzene (Cumene)
p-Isopropyltoluene (p-Cymene)
4-methyl-2-pentanone (MIBK)
Naphthalene
n-Propylbenzene
Styrene
Tetrachloroethene
Trichlorofluoromethane
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
tert-Butyl methyl ether (MTBE)
Toluene
Toluene-d8
Trichloroethene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene (Mesitylene)
o-Xylene
m,p-Xylene
Vinyl acetate
Vinyl chloride
n-Butyl alcohol
Methylcyclohexane

10.2.3.2 Federal Calibration Short List:

Acrolein
Acrylonitrile
Allyl Chloride
Ethyl methacrylate
Isobutyl alcohol
Methacrylonitrile
Methyl methacrylate
Pentachloroethane
Cyclohexanone
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
Tetrahydrofuran
Propionitrile
trans-1,4-Dichloro-2-butene
cis-1,4-Dichloro-2-butene
Benzyl chloride
2-Nitropropane
bis(2-Chloroisopropyl)ether
2-Chloro-1,3-butadiene (Chloroprene)
Ethyl acetate
1,4-Dioxane

10.2.3.3 The Industrial calibration mix contains all of the analytes listed in sections 10.2.3.1 and 10.2.3.2.

10.2.3.4 **Surrogates:** The surrogates used are: Toluene-d8, Dibromo-fluoromethane, and 4-Bromofluorobenzene. Other compounds may be used as surrogates, depending upon the analysis requirements. Final concentrations of the surrogates should be 5 to 50 ug/L. Surrogate analytes are included in the Federal Calibration Long List.

NOTE: SW846 8260B recommends 4 surrogate compounds. In addition to the 3 used by the laboratory, the analyte 1,2-Dichloroethane-d4 is suggested. Since the 1,2-Dichloroethane-d4 peak elutes within one minute of the Dibromo-fluoromethane peak, GEL has elected to exclude one of these compounds. This exclusion should be noted and taken as an exception in response to proposals submitted by Navy clients.

10.2.3.5 **Internal standards:** The volatile internal standards used are Fluorobenzene, Chlorobenzene-d5 and 1,4-Dichlorobenzene-d4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by the GC/MS. Final concentrations of internal standards should be 5 to 50 ug/L.

10.2.3.6 **BFB Tune:** The surrogate solution (50 µg/mL) may be used for BFB tuning resulting in 5 to 50 ng on column.

10.2.4 Calibration Standards: A minimum of five calibration standards is used to establish instrument linearity. Each standard is prepared in a 10 mL or 5 mL Hamilton gas-tight syringe. The lowest concentration level used to standardize the instrument is considered the practical quantitation limit for the compound of interest. (See Appendices 6 and 7 for calibration levels.)

10.2.5 Matrix Spiking/LCS Standards: The spiking solution is a separate source standard from the calibration standards. A set of representative compounds is used to spike sample matrices. Each compound spiked into the sample is reviewed to evaluate the effect of matrix on the spiked compounds.

NOTE: SC DHEC requires that all spiking compound recoveries in the LCS be between 70-130%.

NOTE: For Navy Clients the LCS and matrix spikes will be spiked with all of the analytes on the client target analyte list.

10.2.6 Methanol is screened by "lot" for contaminants prior to use.

10.2.7 Standards will be stored at -10° to (-20°) C.

10.2.7.1 All source standards have a maximum holding time of 12 months from the date received, or the vendor expiration date if sooner. Nongas standards have an expiration of one month from opening. Standards for the permanent gases should be replaced after one week of opening.

10.2.7.2 Intermediate standards have a one week expiration date from the day that they are made, or the vendor expiration date if sooner.

10.2.7.3 Volatile working standards are made up on a daily basis and are never reused the following day.

10.3 Instrumentation:

10.3.1 Purge and Trap system for water and high level soil and waste samples. This system consists of an autosampler, concentrator, and heater assembly.

10.3.1.1 The purging device is designed to accept up to a 25 mL sample volume.

10.3.1.2 The concentrator consists of a trap packed with Tenax/silica gel/charcoal, Vocarb 3000, or equivalent.

10.3.1.4 The heater assembly is used to maintain samples at 40°C.

Recommended Parameters:

10.3.1.5 Standby: 30°C
10.3.1.6 Preheat: 1.0 minute
10.3.1.7 Purge: 11.0 minutes
10.3.1.8 Prepurge: 0.00
10.3.1.9 Sample: 40°C
10.3.1.10 Dry purge: 0.00
10.3.1.11 Desorb preheat: 150°C
10.3.1.12 Desorb: 0.6 minutes at 180°C
10.3.1.13 Bake: 10.00 minutes at 220°C
10.3.1.14 Purge flow: 25 mL/min - 40 mL/min depending upon each instrument
10.3.1.15 Valve: 120°C - Line: 120°C
10.3.1.16 Mount: 120°C
10.3.1.17 2016 valve: 105°C - Line 105°C
10.3.1.18 2032 valve: NI
10.3.1.19 Archon Valve 120°C - Line: 120°C

10.3.2 See SW 846 Method 5035 for purge and trap device for low level soils.

10.3.3 GC/MS System

10.3.3.1 This device consists of a Gas Chromatograph and Mass Selective Detector, capable of scanning from 10 to 800 amu using 70 electron volts in the ionization mode. A computerized data system is used to control or assist in instrument tuning, data acquisition, data reduction, report production, and automation.

10.3.3.2 Columns.

J and W DB 624 fused silica capillary column 0.25mm ID x 60m, 1.4 µm film thickness

J and W DB 624 fused silica capillary column 0.25 mm ID x 30m, 1.4 µm film thickness

J and W DB 624 fused silica capillary column 0.32 mm ID x 60 m, 1.8 µm film thickness (P/N 125-1364) or equivalent

Restek RTX-Volatiles fused silica capillary column 0.25 mm ID x 30m, 1.0 µm film thickness

10.3.3.3 Temperature Limits: -20°C to 260°C

10.3.3.4 Temperature Program: Parameters are instrument dependent.

11.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

11.1 All samples must be stored at 4° ± 2°C from the time of collection until analysis. The samples should be collected and stored with no headspace, however, pea-size bubbles are acceptable. Large volumes of sediment should be noted in the case narrative.

11.2 Large volumes of headspace indicate that the sample was improperly collected. Notify the Project Manager, who is responsible for contacting the client and requesting that the sample be recollected. If recollection is not possible, flag the report to indicate that the samples were improperly collected.

11.3 Samples that contain no headspace have their pH checked with pH paper strips immediately prior to analysis. Aqueous samples are preserved with HCL to a pH of approximately 2 and have a 14-day holding time. Unpreserved waters have a holding time of 7 days from collection.

11.3 Analysts receive the samples directly from the storage cooler. Samples must be tracked into the analyst's custody prior to analysis, then tracked back to the cooler or archiving upon completion of the analysis. If samples are analyzed out of holding the analyst must immediately notify the Group Leader and/or Project Manager and initiate a nonconformance report.

12.0 SAMPLE PREPARATION TECHNIQUES

(For 8260B sample preparation see Section 18.0.)

NOTE: Soils samples originating in South Carolina must be collected and analyzed using EPA Method 5035/8260B.

12.1 For 8260A the samples are allowed to come to ambient temperature and are then analyzed. No preparation is required other than dilutions, if necessary, for low viscosity samples. Solid samples that contain concentrations of analytes greater than the highest concentration level in the calibration or samples with high viscosity, are extracted with methanol, and then diluted in water. Usually 5 g of sample are weighed out and then extracted with 10 mL of methanol. The methanol extract is shaken for two minutes then allowed to settle until distinct layers form. The methanol layer is then decanted and transferred to a 2 mL vial, labeled accordingly, and placed in the sample refrigerator until analysis.

12.1.1 A minimum dilution of 1:50 must be analyzed in order to prevent methanol interference. Maximum volume of methanol analyzed should be 100 µL.

12.1.2 The minimum amount of solid that can be weighed out is 1 gram. If a lower dilution is needed then a serial dilution must be performed on an extract with a weight no less than 1 gram.

12.2 Solid analysis (5030A) - Allow samples to reach room temperature. Weigh approx. 5 grams (+/- 0.1 g) of sample into a 40 mL autosampler vial with a magnetic stir bar. Add 5 mL of organic free water to the vial. Gently shake the sample vial to ensure the magnetic stir bar moves freely. Place the sample vial in the appropriate position and complete the auto-sampler sequence as desired to purge each sample. Add the appropriate volume of surrogate and internal standard solutions. The sample may be diluted by weighing less sample. Do not analyze less than 1.0 gram of the solid sample. If a higher dilution is required, use the methanol extraction method (see section 12.1).

12.3 Aqueous analysis (5030A/B) - Allow samples to reach room temperature. Invert each sample vial to check for headspace. Gently pour approximately 6 mL of the aqueous sample into a 10 mL gas tight syringe with luer-lock end fitting. Use a gloved finger on

the end fitting to stop sample from exiting the syringe. Place the plunger in the syringe and invert, allowing any bubbles to escape through the end fitting. Adjust sample volume to 5 mL by depressing the plunger to the mark. The extraneous sample volume may be added back to the original sample vial or other waste container. Do not decant into the laboratory sinks. Transfer the 5.0 mL of sample to a clean 40 mL auto-sampler vial and place the vial in the appropriate auto-sampler position. Complete the auto-sampler sequence as desired to purge each sample and add the appropriate volume of surrogate and internal standard solutions. After obtaining the aliquot for analysis, use a wide range pH paper, dip the strip into the original sample vial and record the pH in the instrument run log. Indicate on the sample vial with a "X" that the pH strip has been dipped into the sample vial. Analysts should obtain their sample aliquots before taking the pH. In addition, if sample volumes are limited (one vial per sample) the analysts should transfer any remaining sample to a smaller container with no headspace. Analyst should obtain the pH of the sample by pipeting a small volume of the sample across the pH strip into a waste container. Note in batch case narrative any sample discrepancies, i.e. unpreserved sample pHs, headspace (greater than a pea size bubble), excessive sediment.

NOTE: In order to meet the practical quantitation limits in Appendix 7, quality control and client samples use a 10 mL purge volume.

12.4 Spike Analysis

12.4.1 After preparing and prior to purging, fortify the appropriate samples for matrix spike purposes using the appropriate amount of MS/LCS spike solution needed to achieve the desired concentration.

12.4.2 Preserved soils (5035) should be fortified by inserting the syringe needle into the vial septum and injecting the spike solution into the liquid. Tilt the vial during this process to ensure that the spike solution enters the liquid phase of the sample.

12.4.3 Aqueous and/or 5030A solid samples can be fortified in the syringe prior to transferring the aqueous sample or organic free water to the autosampler vial.

12.4.4 Prepare the Laboratory Control Sample (LCS) for solids and liquids by injecting the appropriate amount of spike solution needed to achieve the desired concentration into a gas tight syringe containing organic free water. Transfer the syringe contents to a 40 mL autosampler vial.

13.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Routine Preventative and Special Operational (Failure)

13.1 Preventative maintenance on a GC/MS system involves four basic areas:

13.1.1 Vacuum pumps for the analyzer should have an oil change when the system demonstrates that it is needed. This includes the mechanical, turbomolecular, and/or diffusion pumps. Generally, this occurs once a year.

13.1.2 GC maintenance consists mainly of column and injection port maintenance. These procedures are performed when system sensitivity drops, or air (m/z = 28) is noted present in the system.

13.1.3 Analyzer maintenance is most often usage dependent. The type and quantity of samples that have been injected, determine the frequency of ion source and electron multiplier cleaning and/or replacement.

13.1.4 Autosampler maintenance is very sample dependent. In general, easy maintenance consists of changing the trap and line cleaning. Line cleaning is accomplished by back flushing the system with methanol.

13.2 Non-routine Maintenance Procedures (Special, Operational or Failure Mode Maintenance)

13.2.1 Troubleshooting the autosampler and instrument is a function of analyst experience. In-house service is obtained from GEL's Service Technician. If vendor assistance is needed, then the appropriate vendor is contacted.

13.3 Maintenance logbooks are kept for each instrument and include entries for both routine as well as non-routine maintenance procedures.

14.0 PREPARATION OF STANDARD SOLUTION AND QUALITY CONTROL SAMPLES

14.1 Surrogate Standards: The surrogates used are Toluene-d8, 4-Bromofluorobenzene, and Dibromofluoromethane. A solution of all three surrogates in methanol is purchased from an approved vendor at the appropriate concentration. Other compounds may be used as surrogates depending upon the analysis requirements.

14.2 Internal Standards: The internal standards used are Fluorobenzene, Chlorobenzene-d_5 and 1,4-Dichlorobenzene- d_4. A solution of all three internal standards in methanol is purchased from an approved vendor at the appropriate concentration. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by the GC/MS.

14.3 The standards logbook is used to inventory and record the standards. For guidance on standard documentation, refer to "Laboratory Standards Documentation" (GL-LB-E-007).

15.0 INSTRUMENT CALIBRATION

15.1 Initial Calibration: For method 5035, a calibration curve preserved with sodium bisulfate should be analyzed and used to quantitate all low level soil samples preserved with sodium bisulfate. In addition, an unpreserved calibration curve may be used for high level methanol extracts, waters and low level soils not preserved in sodium bisulfate (frozen preps due to soil reaction with sodium bisulfate). All quality control samples (CVS, LCS, method blanks, and matrix spikes) should be preserved in sodium bisulfate when using the preserved calibration curve.

NOTE: Prior to tuning or running a multi-point calibration, precautions are taken to ensure that the instrument is clean and functioning properly. It is suggested that the standards be set up from low to high in order to prevent carry over. These levels are made in the same volume of DI water for both water multi-point and soil multi-point. (See Appendix 2.)

15.1.1 Establish the GC/MS operating conditions using the following guidelines:

Mass Range: 35 – 300
Scan Time: 0.6 – 2 sec/scan

15.1.2 Calculations: Initial Calibration

15.1.2.1 Tabulate the area response of the characteristic ions against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard

that has a retention time closest to the compound being measured. The RF is calculated as follows:

$$RF = (A_x C_{is}) / (A_{is} C_x)$$

Where:

A_x = Area of the characteristic ion for the compound being measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the specific internal standard.
C_x = Concentration of the compound being measured.

15.1.2.2 The average RF must be calculated for each compound. A system performance check is made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are: Chloromethane, 1,1-Dichloroethane, Bromoform, 1,1,2,2-Tetrachloroethane, and Chlorobenzene. The minimum acceptable average RF for these compounds is: 0.1 for Chloromethane, 1,1-Dichloroethane, and Bromoform, 0.3 for Chlorobenzene and 1,1,2,2-Tetrachloroethane. These compounds typically have RFs of 0.4 - 0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system.

NOTE: All non-SPCC compounds must have a minimum response factor of 0.01, with the exception of poor purging compounds such as Isobutyl alcohol, n-Butyl alcohol, Methyl acetate, and 1,4-Dioxane. For the analysis of Ketones and Carbon Disulfide at a PQL less than 5 ppb, the relative response factor for these analytes must be equal to or greater than 0.05.

Examples of these occurrences are:

- Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.
- Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.
- Tetrachloroethane and 1,1-Dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

15.1.2.3 All newly generated calibration curves should have a secondary review by a Senior Analyst or Data Reviewer before being used.

15.1.3 The internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds during the calibration, the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the Extracted Ion Current Profile (EICP) area for any of the internal standards changes by a factor of two (-50% to +100%) during the calibration, 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 are necessary.

15.1.4 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for Calibration Check Compounds (CCCs) and all target analytes:

$$\%RSD = \frac{SD}{\bar{x}} X\ 100$$

Where:

RSD = relative standard deviation
$\bar{x}$ = mean of initial RFs for a compound
SD = standard deviation of average RFs for a compound

$$SD = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{N - 1}}$$

15.1.4.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range and may be used for quantitation. If the RSD of any target analyte is greater than 15%, then use one of the options in section 15.1.5. A minimum of five calibration standards must be used.

15.1.4.2 The %RSD for each individual CCC must be less than or equal to 30 percent difference. This criterion must be met in order for the individual calibration to be valid. The CCCs are:

- 1,1-Dichloroethene
- Chloroform
- 1,2-Dichloropropane
- Toluene
- Ethylbenzene
- Vinyl chloride

15.1.5 Given the potentially large numbers of analytes that may be analyzed by this method, it is likely that some analytes may exceed the 15% acceptance limits for RSD. In those instances, the following steps may be used:

15.1.5.1 Check the instrument operating conditions. Follow the suggested maintenance procedures in this method to make minor adjustments to the system.

15.1.5.2 Review the results of each standard (area counts, calibration or response factors and RSD) to ensure that the problem is not associated with one of the five initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated.

15.1.5.3 Narrow the calibration range. Remember that changing the lowest level calibration standard will change the practical quantitation limit. Consider the project specifications for regulatory limits and action levels to confirm that this option can be used. Individual analyte end points may be eliminated. However, to eliminate mid-points, the whole standard must be dropped.

15.1.5.4 The analyst may also choose to construct calibration curves of area ratios versus concentration using first order regression fit of the five calibration points. The minimum acceptable correlation coefficient (R) for any compound using linear regression shall be 0.990. The analyst will select only linear regression or average response factor. Higher order curves such as a quadratic curve must never be used.

15.1.6 If the analyst chooses to use linear regression, he/she must not force the calibration line through the origin.

15.1.6.1 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response
a = slope of line (also called the "coefficient of x")
x = concentration of the calibration standard
b = the intercept

15.1.6.2 The analyst should not force the line through the origin, but have the intercept calculated from the data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0, 0) as a sixth calibration point.

15.1.6.3 The regression calculation will generate a correlation coefficient (R_1) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, R must be ≥0.99. The calculated intercept value needs to be evaluated before reporting sample results.

15.1.6.4 A positive value for the intercept indicates that there is some threshold instrument response that is the limiting factor in establishing linearity. A negative intercept value can be transformed into an x-intercept value that represents a threshold concentration that is the limitation. If the intercept is positive, then, as a general rule, results where the instrument response is less than three time (3x) the intercept value may be unreliable. This will afford some protection against false positive results. If the intercept is negative, results below the concentration of the lowest concentration calibration standard may be unreliable.

NOTE: For specific clients, these adjustments to the quantitation limits will apply to all samples analyzed using the regression line.

15.1.6.5 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y - b)}{a}$$

15.1.6.6 Initial calibrations should be verified by the analysis of a second source standard. Complete the analysis of the initial calibration by inserting this standard at the end of the calibration standards. Re-

process this standard using the initial calibration being verified as a continuing calibration standard.. This second source check is used to verify the calibration. High % differences (>20%) should be investigated before the calibration is acceptable.

NOTE: Several Federal clients including the Navy require this calibration verification by second source.)

15.2 Continuing Calibration

15.2.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-Bromofluorobenzene standard into the GC/MS system. The resulting mass spectra for the BFB must meet all of the criteria given in Appendix 3 before sample analysis begins. These criteria must be demonstrated each 12 hour period before samples are analyzed. The mass spectrum of BFB can be obtained using an average of up to three scans and using a background subtraction from within 20 scans before the peak starts or after it ends. However, the analyst may use other documented approaches suggested by the instrument manufacturer.

NOTE: The BFB and continuing calibration verification standard may be combined into a single standard as long as both tuning and calibration criteria for the project can be met without interferences.

15.2.2 The initial calibration curve for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCCs and CCCs. The continuing calibration check standard may be a second source standard. As a second source, it must be obtained from a second supplier. This will determine the validity of the initial calibration on a daily basis.

15.2.3 System Performance Check Compounds (SPCCs): A system performance check must be made every 12 hours. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. The minimum response factors for volatile SPCCs are listed in section 15.1.2.2 of this SOP. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

15.2.4 Calibration Check Compounds (CCCs): After the system performance check is met, CCCs are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{|\overline{RF}_I - RF_c|}{\overline{RF}_I} \times 100$$

Where:

$\overline{RF}_I$ = average response factor from initial calibration
RF_c = response factor from current verification check standard.

If the percent difference for all CCCs is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (>20% difference), corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration will be analyzed.

Passing CCC and SPCC criteria should not be the only factors in evaluating a successful calibration verification. All the analytes in the standard should be evaluated before analysis continues. The laboratory has set a maximum difference/drift of 40% for all non-CCC analytes. If an analyte is flagged as an outlier on the report the analyst should at least evaluate the significance of the flag. The reason for the outlier may be as simple as the computer missing a quant ion, a poor performance compound, or loss of moisture control. Whatever the reason for the flag, all outliers should be evaluated on how the data will be affected by the analytes response. If CCC compounds are not in the target analyte list, the 20% criteria for CCCs may be waived if all the required target analytes are less than 20% difference/drift. In addition, if the CCC and SPCC criteria are met despite these compounds not being required, the required target analytes may have differences/drifts greater than 20%. Again, every standard should be evaluated carefully in order to obtain quality data.

15.2.5 Internal Standard Response: Internal standard areas in the daily continuing calibration verification standard (CCV) must be within +100 to -50% of the initial calibration midpoint internal standard areas and retention times for each internal standard must be within +/- 30 seconds. If internal standards do not meet this criteria, reanalyze the CCV to verify the problem was not random. If the areas fail again, corrective action must be taken. Several actions may correct the problem, i.e., refreshing the internal standard solution on the autosampler, using a newly opened solution, checking instrument conditions have not changed, etc. Document the actions taken to correct the problem in the instrument analysis log.

15.2.6 If the continuing calibration does not meet the aforementioned criteria, the analyst must determine why and take appropriate corrective action. Samples may not be analyzed until the validity of the calibration has been verified.

16.0 INSTRUMENT PERFORMANCE REQUIREMENTS

16.1 Prior to sample analysis, the instrument must pass a BFB (4-bromofluoro-benzene) tune. Tuning criteria are found in Appendix 3. If the instrument does not pass the tune, then the analyst takes corrective action such as manually tuning the instrument and then introducing another BFB tune.

16.2 The instrument must also successfully pass a continuing calibration standard to verify the validity and linearity of the existing multipoint. If the continuing calibration check does not pass (see Section 21.2.2 for criteria) then the instrument may need to be re-calibrated or adjusted. Analyte retention times in the check will not vary by more than 30 seconds from the established retention times at calibration. Peak shapes are examined for excessive tailing or other abnormalities and internal standard areas are checked to ensure that they are not too high or low.

16.3 A matrix blank must also be analyzed and contain no hits of target analytes at or above the reporting value.

17.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

17.1 To ensure that the instrument can generate reliable, accurate data, an analyst must analyze, and successfully pass, a BFB tune, continuing calibration check, and an instrument blank. Hard copies of this data are kept in a folder marked with the instrument # and date.

17.2 Prior to analyzing EPA method 8260B, the analyst should analyze at least four replicates of a QC check standard to establish his or her proficiency at using the method. The analyst should spike the replicates using 50 ppb solution of all volatile organic compounds (second source) in organic free water. Prior to the analysis of these replicates the analyst must pass an acceptable BFB tune check, calibration verification standard, and method blank. The analyst must than calculate the standard deviation and mean recoveries for each analyte. The mean recovery for the replicates must be between 70 – 130%. Due to the large number of analytes in these mixes, it is probable that one or more analytes will fail the recovery criteria. Analyst should recheck the failing data and instrument condition for errors. If there were no errors or instrument problems the analyst should re-perform the replicate analyses for the failing analytes. Repeated failure indicates a general problem with the measurement system. If this occurs, locate and correct the problem and repeat the test for all analytes. This data is filed in the same fashion as other data. For criteria see Section 8, EPA SW-846 Method 8260B, Revision 2, December 1996.

17.3 Method Detection Limits (MDL) are calculated annually. Refer to "Determination of Method Detection Limits" (GL-LB-E-001) for additional information. The results of the MDL studies are maintained as quality records.

17.4 Method precision and accuracy are determined with each batch of samples. The matrix spike and matrix spike duplicate are used to determine the effects of matrix on method precision and accuracy.

18.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

18.1 All calibration and verification standards, blanks, quality control samples, and client samples are analyzed using a heated purge. Ultra Pure helium is bubbled through the sample that is contained in a purging chamber at 40°C. The purgeables are efficiently transferred from the aqueous phase to the vapor phase that is swept through a sorbent where purgeables are trapped. After purging is complete, the trap is heated and backflushed with the inert gas to desorb the analytes onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the analytes that are then detected with a mass spectrometer.

NOTE: A heated 10 mL purge is used to achieve the PQLs listed in Appendix 7.

18.2 Daily GC/MS Analysis Procedure:

18.2.1 At the beginning of each day or 12 hour run window, the GC/MS system is checked to see if acceptable performance criteria are achieved. A 5-50 ng BFB standard is run and must pass before any blank or samples are analyzed. The passing criteria is listed on the tune report. If the tune does not pass, the GC/MS needs to be manually retuned.

18.2.2 If the tune passes, then a calibration verification standard (CVS) is analyzed. This standard is made in water with the surrogates and internals added. The

SPCCs, CCCs minimum response factors and % difference must meet all criteria listed in Section 15.1.6 and 15.2 above. The internal standard response must meet the criteria outlined in Section 15.2.5.

18.2.2.1 If any of the above compounds do not meet the specified criteria, then adjustments need to be made to the instrument and another calibration verification standard analyzed.

18.2.3 All samples and standards solutions are allowed to warm to ambient temperature before analysis.

18.2.3.1 The internal standard areas in each CVS must be within +100 to –50% of the associated midpoint calibration standard, and retention times for each internal standard must be within ± 30 seconds.

18.2.3.2 In addition to the internal standard area/RT check from the calibration verification standard to the midpoint of the current initial calibration, the laboratory also compares the internal areas and retention times of samples and QC to the associated calibration verification standard. If area counts exceed –50 to 100% or retention times are greater than ± 30 seconds, the sample or QC sample must be reanalyzed. If the analyst suspects matrix interference the sample may be diluted to aid in the internal standard recovery.

NOTE: The analyst should be cautious since diluting the sample raises the detection limits. Analysts should seek guidance from a Senior Analyst to ensure that sample data will not be compromised by dilutions.

18.3 Run logs are generated for each analytical batch of samples. There is a separate run log for each instrument. If for some reason a run log cannot be generated, a sequence file from the instrument may be substituted.

18.4 The Mass Selective Detector analyzes minute amounts of material by fragmenting the sample into charged ions, separating them on the basis of molecular weight-to-charge ratio, and then counting the ions as they enter the detector. The counted ions identified by mass can be plotted on a graph with the mass on the x-axis and the counted ions or abundances on the y-axis.

18.5 **Water/Waste Water Preparation and Purge and Trap (SW846 Method 5030B)**

Water analysis is performed by transferring a measured aliquot of sample, in a gas tight syringe, to a 40 mL autosampler vial. The vial is placed in the autosampler where the internal standards and surrogates are added to the sample vial just prior to purging.

18.6 **Low Level Soil Sample Analysis (SW846 5035)**

18.6.1 Using a sampling device (such as an Encore), three sets of approximately 5 grams of soil are collected per sampling site. Two are prepared for Low Level and one for High Level analysis.

18.6.1.1 Prepare two low level samples for analysis

18.6.1.2 Transfer the soil from each Encore device to a tared 40 mL vial containing 5 mL of water, 1 gram of sodium bisulfate and a magnetic stir bar. Reweigh the vial (now containing the soil) and record the weight in the logbook and on the sample label. Store the vials in the refrigerator until analysis.

18.6.1.3 Samples that are received preserved in the field are wiped to remove any extraneous materials from the exterior of the vial. The vial is weighed to the nearest 0.01 gram and the weight is recorded in the logbook. This weight is compared to the weight written on the vial from the field preparation. If any significant changes are detected, the project manager is notified and the appropriate action is taken.

18.6.2 Allow the sample to warm to room temperature. Shake the vial gently to ensure that the contents move freely and that stirring will be effective. Place the vial in the autosampler and ensure that the automatic sampler will add the appropriate volumes of organic-free water, surrogates, and internal standards. All samples, blanks, and calibration standards are analyzed with the same final volume. The autosampler will add 5.0mL of organic-free water, internal standards, and surrogates to all vials set for analysis in the autosampler.

18.6.3 Prior to purging, ensure that the autosampler is set to heat the sample vials to 40° C for 1.0 minutes.

18.6.4 When low level soil analysis produces target analyte results with concentrations higher than the calibration range of the instrument, the sample is reanalyzed by the High Level Method (see 18.7). Such reanalysis need only address those analytes for which the concentration exceeded the calibration range of the Low Level Method.

18.6.5 Results are to be reported on a dry weight basis unless otherwise specified by the client.

18.7 Medium Level Soil Sample Preparation (SW846 5035)

Medium Level soils are collected as stated in Section 18.6.1.

18.7.1 Transfer the soil (approximately 5 grams) from the sampling device to a tared 40mL vial containing 10mL of purge and trap grade methanol. Record the soil weight in the Encore logbook. Using a 25 ul syringe, inject 10 ul of the surrogate solution (2.5 mg/mL) into the methanol/soil mixture. Replace the cap and gently shake for 2 minutes. Allow the soil to settle. Transfer an aliquot of the methanol extract to a 2 mL vial with minimum headspace, label appropriately, and store in the refrigerator until analysis. Discard the remaining soil/extract according to the Laboratory Waste Management Plan.

18.7.2 To analyze the methanol extract transfer 100 ul of the extract to 5 mL gas tight syringe containing organic free water. Transfer the fortified water to an autosampler vial (40 mL voa vial with septum cap). Place the vial in the autosampler and use a predetermined method that adds only the internal standards to the sample vial. Surrogates were added during the extraction step. The addition of 100 µl of methanol extract in 5 mL of water equates to surrogate concentrations of 50 ppb. An additional dilution factor (by using less of the extract) will dilute the surrogate concentrations. Surrogate concentrations are considered "diluted out" with dilution factors greater than 1:10.

18.7.3 For medium levels soils preserved in the field, allow the soil/methanol extract to reach room temperature. Using a long needle syringe, or tilting the vial carefully so not to disturb the soil layer, insert the syringe needle into the vial through the septum cap. Withdraw 100 ul or the desired volume. Transfer the

methanol extract to a gas tight syringe containing 5 mL of organic free water. Transfer the fortified water to an autosampler vial (40 mL voa vial). Place vial in autosampler and use a predetermined method that adds both internal standards and surrogates to the sample vial.

18.7.4 All sample analyses for medium level soils using the methanol extract procedure requires the preparation and analysis of a methanol blank prior to sample analysis. Add 100 ul of purge and trap grade methanol to a gas tight syringe containing 5 mL of organic free water. Transfer the water to an autosampler vial (40 mL voa vial). Place the vial in the autosampler and use a predetermined method that adds both internal standards and surrogates to the sample vial. Low Level Soil Sample Analysis (SW846 5030A)

18.8 Low Level Soil Analysis (SW846 5030A as part of 8260A)

NOTE: Low-level soil samples originating in South Carolina must be collected and analyzed using EPA Method 5035.

18.9 Low level soil analysis is performed by weighing out 5g of sample into a tared 40 mL vial containing a stir bar. The vial is then sealed and loaded in the autosampler. (Use a predetermined method to add 10 mLs of water, internal standards and surrogates to the sample vial.)

18.10 Medium Level Soil Sample Analysis (SW846 5030A)

Medium level soil analysis is performed by weighing out 5g of sample into 10 mL methanol in a tared 40 mL vial. Replace the cap and gently shake for 2 minutes. Allow soil to settle. Transfer an aliquot of the methanol extract to a 2 mL vial with minimal head space, label appropriately, and store in the refrigerator until analysis. Discard the remaining soil/extract in the appropriate manner for solvent/solid waste per GL-LB-E-011 for laboratory waste disposal.

18.11 Samples can be placed on the autosampler and then programmed to run automatically.

18.12 Once samples are loaded onto the autosampler, the order in which they are to be analyzed is programmed and the sequence is initiated.

19.0 CALCULATIONS AND DATA REDUCTION METHODS

19.1 Qualitative Analysis:

19.1.1 A compound is identified by:

19.1.1.1 A comparison of the sample mass spectrum with the mass spectrum of a standard reference of the suspected compound. Mass spectrum for standard reference must be obtained on the user's GC/MS. The NIST Library is used as reference.

19.1.1.2 Elution of sample component at the same GC relative retention time (RRT) as those of the standard component.

19.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

19.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of

the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

19.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample, appropriate selection of analyte spectra and background spectra is important.

19.1.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra and in the qualitative identification of compounds. When analytes coelute, the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

19.1.2 The sample component RRT must compare within ± 30 seconds of the RRT of the standard component, run in the same 12 hour period. If coelution of another compound prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the components of interest. Pay close attention to the following compounds for possible coelution and identification: 1,1,1-trichloroethane, and carbon tetrachloride; m,p-xylenes and ethylbenzene; the three dichlorobenzene isomers; chloromethane and dichlorodifluoromethane, cis-1,2-dichloroethene and trans-1,2-dichloroethene; cis-1,3-dichlorpropene and trans-1,3-dichloropropene; 2-chlorotoluene and 4-chlorotoluene; the two trimethylbenzenes; the three butylbenzenes; and the two trichlorobenzenes.

19.1.3 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analysis being conducted. Use the following guidelines for making tentative identifications:

19.1.3.1 Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

19.1.3.2 The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30% and 70%.)

19.1.3.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

19.1.3.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

19.1.3.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks.

19.2 For example calculations which relate calibration methods, response factors, etc. to calibration curves refer to section 21.

19.3 Quantitative Analysis

$$RF = \frac{(A_T)}{(A_{IS})} \times \frac{(C_{IS})}{(C_T)}$$

Where:

RF = response factor
A_{IS} = area of internal standard
C_T = concentration of target analyte
A_T = area of target analyte
C_{IS} = concentration of internal standard

19.3.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of a given analyte.

19.4 The concentration of each identified analyte in the sample is calculated as follows:

Water and Water-Miscible Waste:

$$\text{Concentration } (\mu g/L) = [(A_x)(C_{is})(V_O)] / [(A_{is})(RRF)(V_i)]$$

Where:

A_x = Area of characteristic ion of compound being measured
C_{is} = Concentration of internal standard purged in µg/L
A_{is} = Area of characteristic ion for the internal standard
RRF = Relative Response factor for compound being measured (see above)
V_o = Total Purge Volume (mL)
V_i= Volume of sample purged (mL)

Sediment/Soil, Sludge, and Waste

High Level:

$$\text{Concentration } (\mu g/kg) = [(A_x)(C_{is})(V_t)(V_o)] / [(A_{is})(RF)(W_s)(V_i)]$$

Low Level:

$$\text{Concentration } (\mu g/kg) = [(A_x)(C_{is})(V_O)] / [(A_{is})(RF)(W_s)]$$

Where:

A_x, C_{is}, A_{is}, RF = same as for water
V_t = Volume of total extract (use 10,000 µL or a factor of this when dilutions are made.)
V_i = Volume of extract added (µL) for purging
W_s = Weight of sample extracted or purged (g). The wet or dry weight may be used, depending upon the specific applications of the data.
V_O = Total Purge Volume (mL)

19.4.1 Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis.

19.4.2 Where applicable, an estimate of concentration for non-calibrated components in the sample is made. The formulas given above shall be used with the following modifications: The areas A_x and A_{is} shall be from the total ion chromatograms, and the RF for the compound shall be assumed to be 1.

19.4.2.1 The concentration obtained is an indication that the value is an estimate, and identifies which internal standard was used to determine concentrations. Use the nearest internal standard free of interferences.

19.4.3 When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

19.5 Results are reported to three significant figures.

19.6 Data is reported in units of µg/L or ppb for waters, and µg/kg or ppb for soils and sludges. (See Appendix 4 for detailed information on significant figures.)

19.7 All data is stored by Work Order number in filing cabinets in the lab. The data is also "backed up" on ALPHA LIMS.

20.0 DATA RECORDING

Data is recorded as a quantitation report that is generated by the computer system. All calculations and comments are recorded directly on the quantitation reports.

21.0 QUALITY CONTROL REQUIREMENTS

21.1 Frequency of Quality Control Activities

21.1.1 Initial and Continuing Calibration

21.1.1.1 Before the analysis of any blanks, spikes or samples, the instrument must be calibrated. This multilevel initial calibration is used to establish the linearity of the instrument for the analytes of interest. Once this calibration is in place, the frequency thereafter is determined from the analysis of continuing calibration standards.

21.1.1.2 In method 8260B/A, the continuing calibration standard is also used to verify the instrument calibration compared to the last multilevel calibration analyzed. However, when performing analysis according to the protocol set down by this method, the continuing calibration check must be performed every 12 hours.

21.1.2 Blank Analysis

21.1.2.1 Method Blanks are used to determine background (laboratory) concentrations of target analytes that have the potential of interfering with sample analysis. For method 8260B/A, a blank is analyzed with each analytical sequence.

21.1.2.2 Other types of blanks can be used to determine possible contamination from various points in the process. Trip Blanks can be used for evaluating the bottles in which the samples are collected. Field Blanks are used to discover potential interferences that may originate from the collection process. The frequency at which such blanks are analyzed are determined by the client (internal or external). Refrigerator or Storage Blanks are analyzed on at least a weekly basis to determine the cleanliness of the storage area.

21.1.3 Spike and Duplicate Analysis

21.1.3.1 Accuracy is monitored through the analysis of sample spikes. Matrix spikes are performed for every Quality Control batch up to a maximum of 20 samples of similar matrix.

21.1.3.2 Precision is monitored through the analysis of duplicates. For method 8260B, the matrix spike or sample is duplicated. This ensures the availability of two sets of results for comparison.

21.1.4 Laboratory Control Samples (LCS) are used to determine if the process is in control. If a matrix spike fails due to matrix related interference, then the analysis of the LCS demonstrates that the instrument is in control. The continuing calibration check (CCV) may be used as an LCS if it is a second source standard. Analyze the LCS in each 12 hour sequence. The LCS may be analyzed before the method blank as the CCV.

21.1.5 Surrogate spikes must be added to all standards, blanks, spikes, duplicates, and samples.

21.2 Acceptance Limits for Quality Control Activities

21.2.1 Initial Calibration

21.2.1.1 Although initial calibration includes all analytes of interest, the criteria for acceptance for method 8260B/A is based on System Performance Check Compounds (SPCC) and Calibration Check Compounds (CCC). The average response factor (RF) for the five levels are calculated for each of the SPCCs (Chloromethane, 1,1-Dichloroethane, Bromoform, 1,1,2,2-Tetrachloroethane, and Chlorobenzene). The minimum acceptable average RF for these compounds is: 0.1 for Chloromethane and 1,1-Dichloroethane and Bromoform, 0.3 for Chlorobenzene and 1,1,2,2-Tetrachloroethane. The percent relative standard deviation (%RSD) must be calculated for using each level for all the CCCs. The %RSD for each individual CCC (1,1-Dichloroethene, Chloroform, 1,2-Dichloropropane, Toluene, Ethylbenzene, and Vinyl chloride) must be less than thirty percent (30%). In order to quantitate samples the analytes average % RSD must be less than 15%. See section 15 for all calibration criteria.

$$RF = \frac{(A_X C_{IS})}{(A_{IS} C_X)}$$

Where:

A_X = Area of the characteristic ion for the compound being measured

C_{IS} =Concentration of the specific internal standard

A_{IS} =Area of the characteristic ion for the specific internal standard

C_X = Concentration of the compound being measured

$$\%RSD = \frac{SD}{\bar{x}} X\ 100$$

Where:

RSD = relative standard deviation

$\bar{x}$ = mean of 5 initial RFs for a compound

SD = standard deviation of average RFs for a compound

$$D = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1}}$$

21.2.2 Continuing Calibration

21.2.2.1 When analyzing samples by method 8260B/A, the instrument calibration must be verified every 12 hours through the analysis of a continuing calibration standard. Although this standard contains every analyte of interest, the criteria for acceptability are based on the CCCs and SPCCs. The criteria for the SPCCs are the same as for the initial calibration (see section 21.2.1.1). The percent difference must be less than 20% for each CCC.

$$\% \text{ Difference} = \frac{|\overline{RF}_i - RF_c|}{\overline{RF}_i} \times 100$$

Where:
$\overline{RF}_i$ = Average response factor from initial calibration
RF_c = Response factor from current calibration check standard

21.2.3 Method blank criteria requires that concentrations of all analytes of interest must be below the client reporting limit. Ideally, all target analyte concentrations should be below the laboratory method detection limit, however, concentrations below reporting limits are acceptable. The analyst should take corrective action to ensure that target analytes do not exceed the reporting limits.

21.2.4 Matrix Spikes/Duplicates.

21.2.4.1 The 8260B/A criteria for both matrix spikes and matrix spike duplicates will be statistically determined after the analysis of 20 to 30 matrix pairs. Accuracy and precision data from Tables 6, 7, and 18 should be used as guidance. If data is not available for specific compounds, a guidance of 70 - 130% recovery for spikes.

21.2.4.2 The criteria for sample duplication when analyzing samples using method 8260B/A are that any target present over five (5) times the detection limit must be within ±20% of each other. As a statistical database is built, statistical process control (SPC) limits are generated.

21.2.5 A laboratory control sample **must** be analyzed in every 12-hour analytical sequence. Statistical control limits for each compound should be derived after the analysis of up to 20 to 30 LCSs (per matrix, annually).

NOTE: For SC DHEC, if SPC limits are wider than 70-130%, the LCS acceptance criteria shall default to 70-130% for spiked analytes in the LCS solution.

21.2.6 The three surrogates used in Method 8260B/A are: Tolulene-d8, 4-bromofluorobenzene, and dibromofluoromethane. The criteria are determined statistically at least annually utilizing a minimum of 20 data points. The method suggested recovery is 70 - 130%. These values will change as the data base becomes large enough to generate SPC limits.

21.3 Nonconformance

21.3.1 When analyzing a multi-point calibration for many analytes at once, the chances are high that a few may not meet the criteria. Additional standards for just the compounds not meeting may be reanalyzed. If they still do not meet the requirements, the instrument may need maintenance before continuing or new standards may be needed.

21.3.2 If the continuing calibration fails any of the criteria in Section 21.2.2, the analyst must take action to correct the situation. This may be retuning, reanalyzing the standard, adjusting the purge flow, or any number of maintenance practices in order to meet the daily calibration. If all attempts fail, the analyst must analyze a new series of multi-point calibration standards.

21.3.3 When the blank fails the criteria defined in Section 21.2.3, the analyst must find and eliminate the source of contamination before proceeding with the analyses. Another blank must be run before samples can be analyzed.

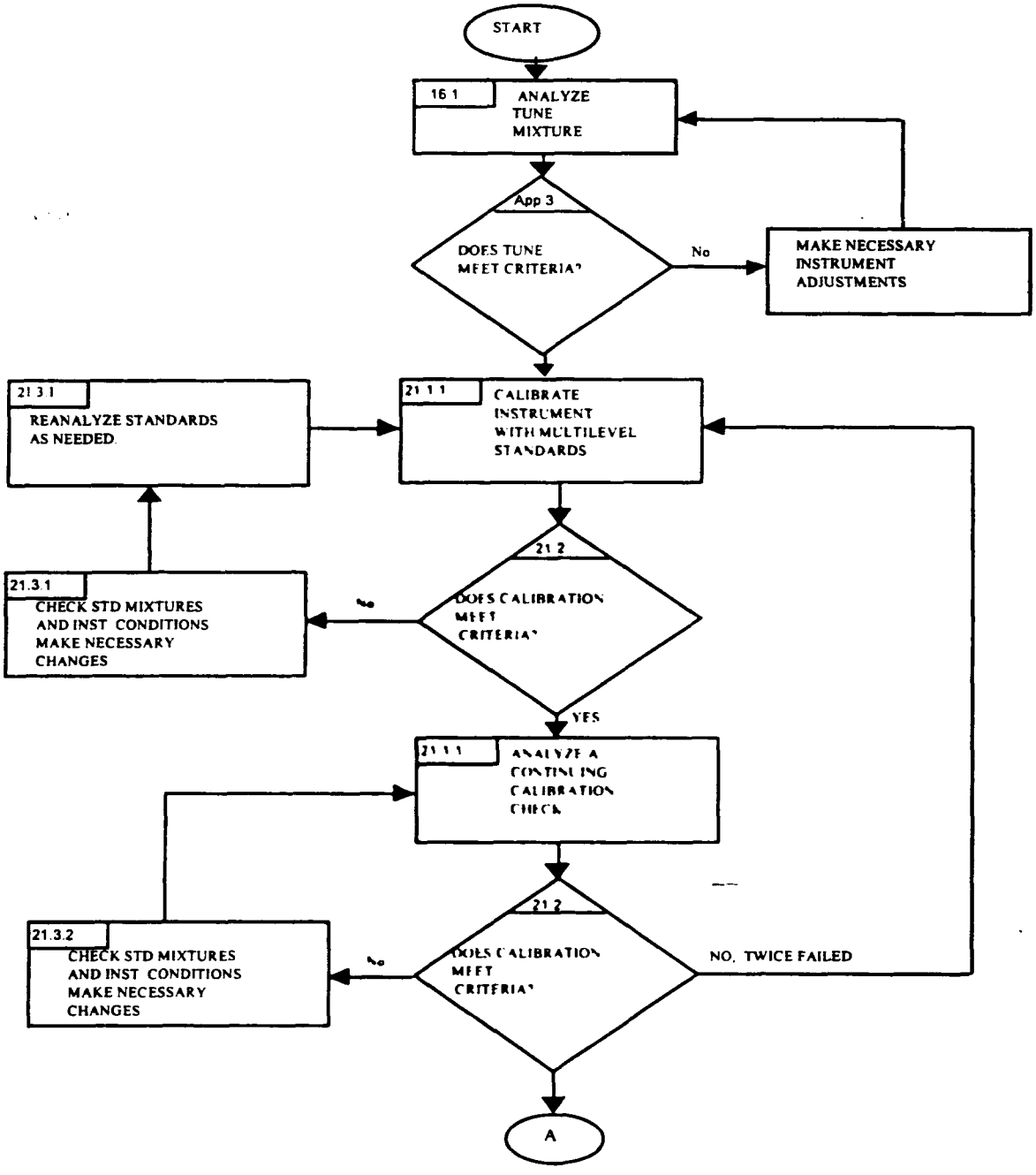
21.3.4 If any surrogate out of the three fails the criteria in Section 21.2.6, the sample must be reanalyzed. If the surrogates fail a second time, in the same manner, and the blank and LCS recoveries do not indicate a system problem, the failure is attributed to matrix effects.

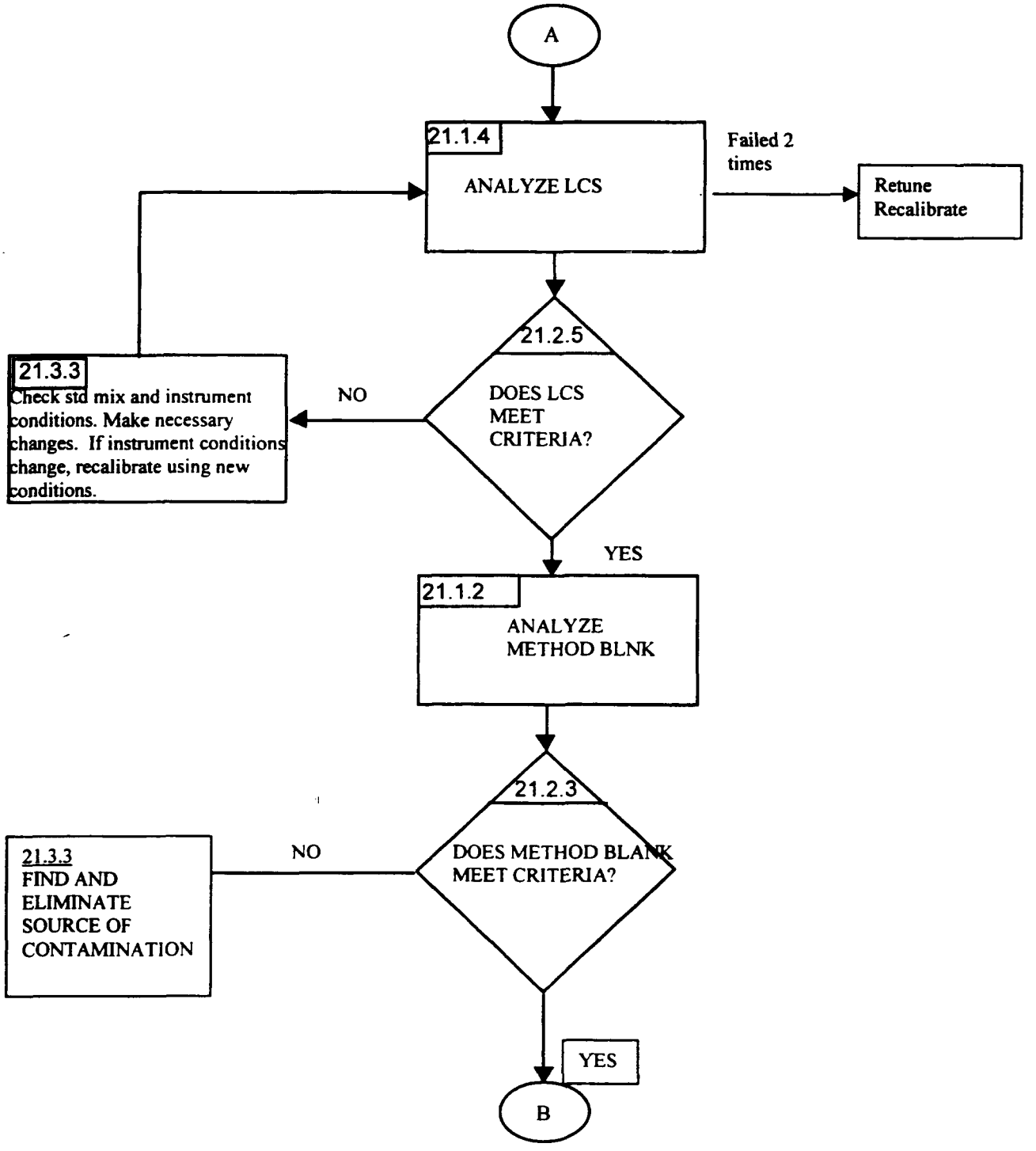
21.3.5 For SC DHEC, the laboratory monitors the recoveries of a representative group of analytes from the total analyte list for control purposes. All analyte recoveries in the LCS should meet recovery limits of 70-130%. . If any of these analyte recoveries are outside the LCS limits, the analysis should stop and corrective action should be attempted before continuing with the analysis. Corrective action may include repeating the analysis, opening a new spike mix and reanalyzing, or more complex actions may be attempted. If re-tuning the instrument, the analyst must analyze a tune check (BFB) and calibration verification standard before reanalyzing the LCS.

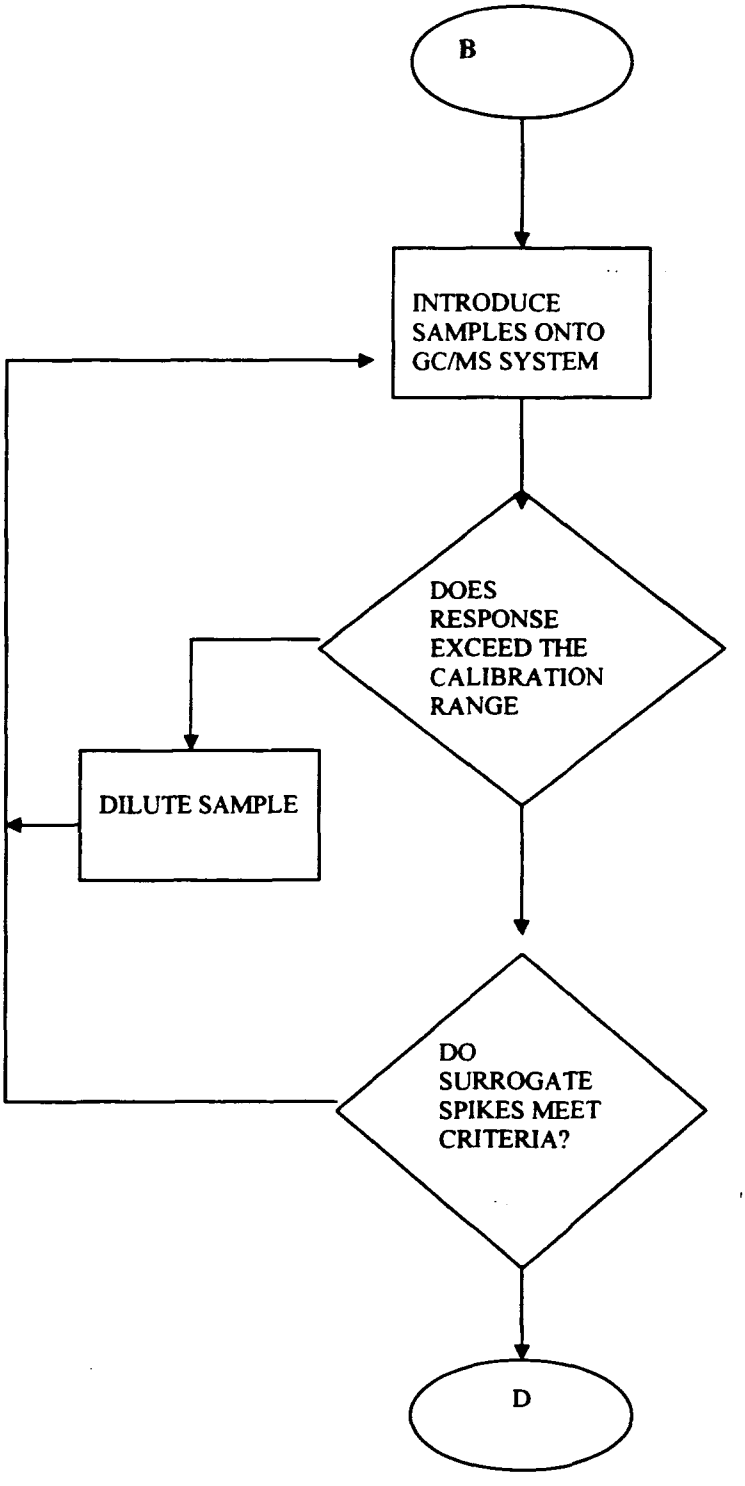
NOTE: Most federal clients (Navy, DOE, DOD) require the laboratory to spike all target analytes of interest in the LCS. The laboratory should develop SPC limits for each analyte. Reporting requirements for the LCS should be stated per client contract.

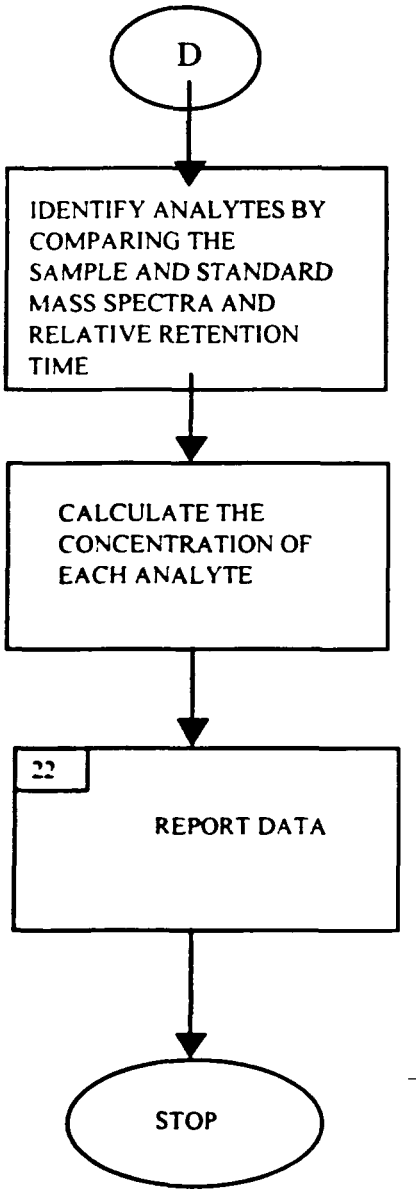
21.4 The manner in which data will be accepted or rejected is described in the flowchart in Figure 1.1.

FIGURE
1.1


START
16.1
ANALYZE TUNE MIXTURE
App 3
DOES TUNE MEET CRITERIA?
No
MAKE NECESSARY INSTRUMENT ADJUSTMENTS
21.3.1
REANALYZE STANDARDS AS NEEDED.
21.1.1
CALIBRATE INSTRUMENT WITH MULTILEVEL STANDARDS
21.2
DOES CALIBRATION MEET CRITERIA?
21.3.1
CHECK STD MIXTURES AND INST CONDITIONS MAKE NECESSARY CHANGES
YES
21.1.1
ANALYZE A CONTINUING CALIBRATION CHECK
21.2
DOES CALIBRATION MEET CRITERIA?
NO, TWICE FAILED
21.3.2
CHECK STD MIXTURES AND INST CONDITIONS MAKE NECESSARY CHANGES
A


A
21.1.4
ANALYZE LCS
Failed 2 times
Retune
Recalibrate
21.2.5
DOES LCS MEET CRITERIA?
NO
21.3.3
Check std mix and instrument conditions. Make necessary changes. If instrument conditions change, recalibrate using new conditions.
YES
21.1.2
ANALYZE METHOD BLNK
21.2.3
DOES METHOD BLANK MEET CRITERIA?
NO
21.3.3
FIND AND ELIMINATE SOURCE OF CONTAMINATION
YES
B


B
INTRODUCE SAMPLES ONTO GC/MS SYSTEM
DOES RESPONSE EXCEED THE CALIBRATION RANGE
DILUTE SAMPLE
DO SURROGATE SPIKES MEET CRITERIA?
D



21.5 SPC limits are determined by criteria set forth in EPA Method 8000B. For a given matrix, calculate the upper and lower control limit for method performance for each standard of interest as follows:

Upper control limit (UCL) = p + 3 s
Lower control limit (LCL) - p - 3 s

Where:

p = Average percent recovery
s = Standard deviation of percent recovery

21.6 In addition to the quality control requirements described above, each GC/MS system must be demonstrated to meet the tune criteria listed in Appendix 3 for Bromofluorobenzene every 12 hours.

22.0 DATA REVIEW, VALIDATION AND APPROVAL PROCEDURES

22.1 All data must be reviewed by another analyst before it is reported. The reviewer must check the data report against the raw data and verify the validity and accuracy of the data.

22.2 All data is reviewed in a batch before that batch is sent to "DONE".

22.3 The levels of review responsibility are:

22.3.1 First level review: The analyst must ensure the overall quality of the data. Included in this review are: the BFB tune criteria, samples within tune time, calibration verification standard check, method blank, matrix spikes, laboratory control sample, surrogate recovery, internal standard response, over range concentrations include a dilution, reanalyses as required, manual integrations are appropriate and correct.

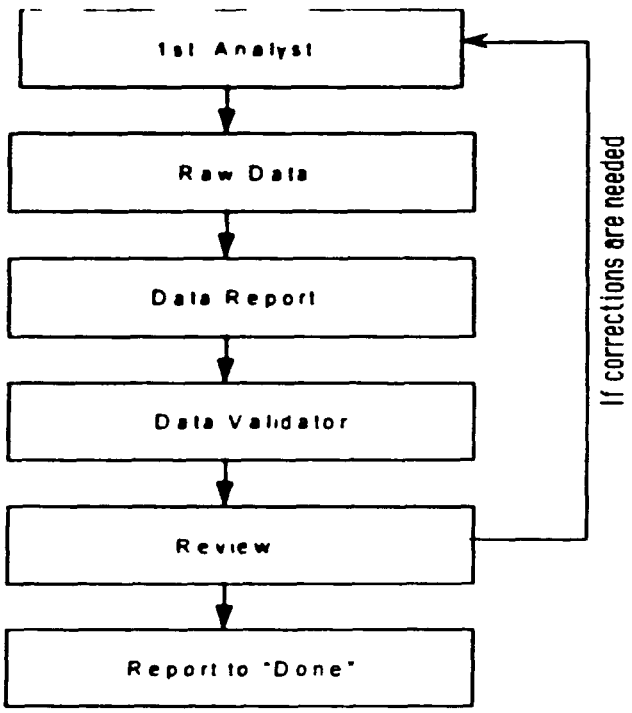
22.3.2 Second level review: A peer must review all of the data before it can be released from the lab. The peer performs all of the checks that the first analyst did and compares the data with the run log. Particular attention must be paid to the 12 hour tune window, the check standard, and internal standard area counts. All hits must also be reviewed very carefully. When the second level review is complete, the peer reviewer initials the data.

22.4 Items checked in the first level review are the tune, continuing calibration, blanks, spikes, spike duplicates, and each sample. In each sample the dilution is verified, surrogates are checked, and each hit is checked to verify its validity and accuracy.

22.6 In addition, the reviewer initials the checked data report.

22.7 All raw data, along with a copy of the data report and the run log, is needed to complete the review process.

22.8 A flow chart showing the process by which papers and documents undergo review follows:



23.0 DATA TRANSMITTAL

After the data has been peer reviewed and is ready for reporting, the report is sent to "DONE."

24.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

19.1 All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

19.2 All standards are recorded in ALPHA LIMS.

25.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper handling and disposal of sample and reagent wastes from this procedure, refer to the "Laboratory Waste Management Plan" (GL-LB-G-001).

APPENDIX 1

(For Illustrative Purposes Only)

METHOD 8260B VOLATILE ANALYTES

Ethyl Acetate
Dichlorodifluoromethane
Chloromethane
Vinyl Chloride
Bromomethane
Chloroethane
Trichlorofluoromethane
Acrolein
Acetone
1,1-Dichloroethene
Iodomethane
Carbon Disulfide
Methylene Chloride
Acrylonitrile
trans-1,2-Dichloroethene
Vinyl Acetate
1,1-Dichloroethane
2,2-Dichloropropane
cis-1,2-Dichloroethene
Bromochloromethane
2-Butanone(MEK)
Chloroform
1,1,1-Trichloroethane
1,2-Dichloropropane
1,1-Dichloropropene
Carbon Tetrachloride
Benzene
2-Chloroethylvinyl ether
trans-1,3-Dichloropropene
Trichloroethene
Dibromomethane
cis-1,3-Dichloropropene
4-Methyl-2-pentanone (MIBK)
Toluene
1,1,2-Trichloroethane
1,2-Dibromoethane
2-Chloro-1,3-butadiene (chloroprene)
Methacrylonitrile
Pentachloroethane
Isobutyl alcohol
cis-1,4-Dichloro-2-butene
2-Nitropropane
1,2-Dichloroethane
1,4-Dioxane
Methyl tert-butyl ether (MTBE)
Cyclohexane
Methyl cyclohexane
1,1,2-Trichloro-1,2,2-Trifluoroethane
1,3-Dichloropropane
2-Hexanone
Dibromochloromethane
Tetrachloroethene
Chlorobenzene
1,1,1,2-Tetrachloroethane
Ethylbenzene
m,p-Xylenes
Bromoform
Styrene
o-Xylene
1,1,2,2-Tetrachloroethane
Isopropylbenzene
Bromobenzene
1,2,3-Trichloropropane
n-Propylbenzene
2-Chlorotoluene
1,3,5-Trimethylbenzene
4-Chlorotoluene
tert-Butylbenzene
1,2,4-Trimethylbenzene
sec-Butylbenzene
Isopropyltoluene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
n-Butylbenzene
1,2-Dichlorobenzene
1,Dibromo-3-chloropropane
1,2,4-Trichlorobenzene
Hexachlorobutadiene
Naphthalene
1,2,3-Trichlorobenzene
Bromodichloromethane
Acetonitrile
Allylchloride
Ethyl methacrylate
Methyl methacrylate
trans-1,4-Dichloro-2-butene
Propionitrile
Benzyl Chloride
bis(2-chloroisopropyl)ether
Ethyl ether
Cyclohexanone
n-butanol
Methyl acetate
Tetrahydrofuran

APPENDIX 2
(For Illustrative Purposes Only)

Calibration Mixes

Conc.	0.5ppm	1.0ppm	2.0ppm	5.0ppm	10ppm	20ppm	50ppm	100ppm	200ppm
0.2ppb	4µl/10ml								
0.5ppb		5µl/10ml							
1.0ppb		5µl/5ml	5µl/10ml						
2.0ppb			5µl/5ml	4µl/10ml					
5.0ppb				5µl/5ml	5µl/10ml				
10ppb					5µl/5ml	5µl/10ml			
20ppb						5µl/5ml	4µl/10ml		
50ppb							5µl/5ml	5µl/10ml	
100ppb								5µl/5ml	5µl/10ml

APPENDIX 3

BFB MASS - INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

Mass	Intensity Required (relative abundance)
50	15-40% of mass 95
75	30-60% of mass 95
95	base peak, 100% relative abundance
96	5-9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5-9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5-9% of mass 176

APPENDIX 4

(For Illustrative Purposes Only)

Significant Figures

Significant figures in a measurement are defined as all the digits which are known with certainty plus one final digit which is estimated. It is acceptable, and in fact, advisable, to carry all of the digits during intermediate calculations. However, only the significant figures should be reported in the final result.

Several basic rules will help you report only significant figures.

1: Addition and Subtraction

In the case of whole numbers, note the number that contains the fewest number of significant figures and retain this number of significant figures in the answer.

In the case of decimal fractions, note the number that contains the fewest digits to the right of the decimal point and retain this number of digits in the answer.

Example:

```
          10.90
         100.1
           0.485
         111.485
Report   111.5
```

2. Multiplication and Division

The number of significant figures retained in the result of a multiplication or division calculation is determined by the precision of the individual measurements, not by the number of significant figures in the measurements.

Example: Consider the multiplication of two numbers, 87.75 and 43.

The product of 87.75 and 43 is 2,773.25.
The precision of 87.75 is ± 0.01 in 87.75 or 0.01%.
The precision of 43 is ± 1 in 43 or 2.3%.
Therefore the result should be rounded to reflect a precision as close to 2.2% as possible.
If we round to 3,773 the implied precision is ± 1 in 3,773 or 0.03%.
If we round to 3,770 the implied precision is ± 10 in 3,770 or 0.26%.
If we round to 3,800 the implied precision is ± 100 in 3,8000 or 2.6%.
The result of this calculation should be reported correctly then as 3,800.

3. Zeros

All trailing zeros to the right of the decimal point are considered to be significant. If a zero to the left of the decimal point is significant, it should be followed immediately by the decimal point. Use scientific notation if necessary in this case to place the decimal point. Example:

300 no zeros are significant
300 both zeros are significant
3.0×10^2 one zero is significant

A zero should always be placed to the left of a decimal fraction simply to reassure the reader that the decimal is intended, however, this zero is not considered to be a significant figure.

4. Rounding: Three rules apply to rounding.

a: If the number to be rounded is greater than 5, round up.
For example, 476 rounded to two significant figures is 480.

b: If the number to be rounded is less than 5, round down.
For example, 474 to two significant figures is 470.

c: If the number to be rounded is equal to 5, always round to an even number.
For example, 475 rounded to two significant figures is 480 while 465 rounded to two significant figures is 460.

5. ALPHA LIMS automatically reports three significant figures.

APPENDIX 5

(For Illustrative Purposes Only)

SURROGATE SPIKE RECOVERY LIMITS FOR
WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/High Water	Low/High Soil/Sediment
4-Bromofluorobenzene[a]	70 – 130	70 - 130
Dibromofluoromethane[a]	70 – 130	70 - 130
Toluene-d_8[a]	70 – 130	70 - 130

[a]Limits are taken from reference SW-846 Method 8000B.
The limits will change when data from 20 or more analyses are calculated.

APPENDIX 6

SW846 8260B/EPA 624 CALIBRATION STANDARD CONCENTRATION LEVELS

	Level 1*	Level 2	Level 3	Level 4	Level 5	Level 6 #	Level 7
Fluorobenzene (IS)							
Dibromofluoromethane (surr)	1	2	5	10	20	50	100
Dichlorodifluoromethane	1	2	5	10	20	50	100
Chloromethane	1	2	5	10	20	50	100
Vinyl chloride	1	2	5	10	20	50	100
Bromomethane	1	2	5	10	20	50	100
Chloroethane	1	2	5	10	20	50	100
Trichlorofluoromethane	1	2	5	10	20	50	100
1,1-Dichloroethene	1	2	5	10	20	50	100
Acetone	5	10	25	50	100	250	500
Iodomethane	5	10	25	50	100	250	500
Carbon disulfide	5	10	25	50	100	250	500
Acetonitrile	25	50	125	250	500	1250	2500
Methylene chloride	1	2	5**	10	20	50	100
trans-1,2-Dichloroethene	1	2	5	10	20	50	100
1,1-Dichloroethane	1	2	5	10	20	50	100
Vinyl acetate	5	10	25	50	100	250	500
cis-1,2-Dichloroethene	1	2	5	10	20	50	100
2,2-Dichloropropane	1	2	5	10	20	50	100
2-Butanone	5	10	25	50	100	250	500
Bromochloromethane	1	2	5	10	20	50	100
Chloroform	1	2	5	10	20	50	100
1,1,1-Trichloroethane	1	2	5	10	20	50	100
1,1-Dichloropropene	1	2	5	10	20	50	100
Carbon tetrachloride	1	2	5	10	20	50	100
Benzene	1	2	5	10	20	50	100
1,2-Dichloroethane	1	2	5	10	20	50	100
Trichloroethene	1	2	5	10	20	50	100
1,2-Dichloropropane	1	2	5	10	20	50	100
Dibromomethane	1	2	5	10	20	50	100
Bromodichloromethane	1	2	5	10	20	50	100
2-Chloroethylvinylether	5	10	25	50	100	250	500
cis-1,3-Dichloropropene	1	2	5	10	20	50	100
2-Nitropropane	5	10	25	50	100	250	500
Ethyl acetate	5	10	25	50	100	250	500
Acrolein	10	20	50	100	200	500	1000
Trichlorotrifluoroethane	5	10	25	50	100	250	500
Allyl chloride	5	10	25	50	100	250	500
Acrylonitrile	10	20	50	100	200	500	1000
1,4-Dioxane	50	100	250	500	1000	2500	5000
tert-Butylmethylether	1	2	5	10	20	50	100
Isobutyl alcohol	50	100	250	500	1000	2500	5000
Methacrylonitrile	5	10	25	50	100	250	500
Propionitrile	5	10	25	50	100	250	500
Methyl methacrylate	5	10	25	50	100	250	500
2-Chloro-1,3-butadiene(chloroprene)	1	2	5	10	20	50	100
Ethyl ether	1	2	5	10	20	50	100
n-Butyl alcohol	50	100	250	500	1000	2500	5000

Chlorobenzene-d5 (IS)							
Toluene-d8 (surr)	1	2	5	10	20	50	100
4-Methyl-2-pentanone	5	10	25	50	100	250	500
Toluene	1	2	5	10	20	50	100
trans-1,3-Dichloropropene	1	2	5	10	20	50	100
1,1,2-Trichloroethane	1	2	5	10	20	50	100
Tetrachloroethene	1	2	5	10	20	50	100
1,3-Dichloropropane	1	2	5	10	20	50	100
2-Hexanone	5	10	25	50	100	250	500
Dibromochloromethane	1	2	5	10	20	50	100
1,2-Dibromoethane	1	2	5	10	20	50	100
Chlorobenzene	1	2	5	10	20	50	100
1,1,1,2-Tetrachloroethane	1	2	5	10	20	50	100
Ethylbenzene	1	2	5	10	20	50	100
m,p-Xylene	2	4	10	20	40	100	200
o-Xylene	1	2	5	10	20	50	100
Stryene	1	2	5	10	20	50	100
Cyclohexanone	50	100	250	500	1000	2500	5000
Ethyl methacrylate	5	10	25	50	100	250	500
1,4-Dichlorobenzene-d4 (IS)							
Bromofluorobenzene (surr)	1	2	5	10	20	50	100
Bromoform	1	2	5	10	20	50	100
Isopropylbenzene	1	2	5	10	20	50	100
1,1,2,2-Tetrachloroethane	1	2	5	10	20	50	100
Bromobenzene	1	2	5	10	20	50	100
1,2,3-Trichloropropane	1	2	5	10	20	50	100
n-Propylbenzene	1	2	5	10	20	50	100
2-Chlorotoluene	1	2	5	10	20	50	100
1,3,5-Trimethylbenzene	1	2	5	10	20	50	100
4-Chlorotoluene	1	2	5	10	20	50	100
1,2,4-Trimethylbenzene	1	2	5	10	20	50	100
sec-Butylbenzene	1	2	5	10	20	50	100
1,3-Dichlorobenzene	1	2	5	10	20	50	100
tert-Butylbenzene	1	2	5	10	20	50	100
Isopropyltoluene	1	2	5	10	20	50	100
1,4-Dichlorobenzene	1	2	5	10	20	50	100
n-Butylbenzene	1	2	5	10	20	50	100
1,2-Dichlorobenzene	1	2	5	10	20	50	100
1,2-Dibromo-3-chloropropane	1	2	5	10	20	50	100
1,2,4-Trichlorobenzene	1	2	5	10	20	50	100
Hexachlorobutadiene	1	2	5	10	20	50	100
Naphthalene	1	2	5	10	20	50	100
1,2,3-Trichlorobenzene	1	2	5	10	20	50	100
cis-1,4-Dichloro-2-butene	5	10	25	50	100	250	500
trans-1,4-Dichloro-2-butene	5	10	25	50	100	250	500
Tetrahydrofuran	5	10	25	50	100	250	500
Pentachloroethane	5	10	25	50	100	250	500
Benzyl chloride	5	10	25	50	100	250	500
bis(2-Chloro-isopropyl)ether	5	10	25	50	100	250	500

* Laboratory Practical Quantitation Limits (PQL) except for Methylene

** PQL for Methylene chloride

# Indicates calibration verification concentration level

APPENDIX 7

EPA 524.2/Low level SW846 8260B
Calibration Standard Concentration Levels

	Level 1*	Level 1a*	Level 2	Level 3	Level 4 #	Level 5	Level 6	Level 7
Fluorobenzene (IS)								
Dibromofluoromethane (surr)		0.5	1	2	5	10	50	100
Dichlorodifluoromethane		0.5	1	2	5	10	50	100
Chloromethane		0.5	1	2	5	10	50	100
Vinyl chloride		0.5	1	2	5	10	50	100
Bromomethane		0.5	1	2	5	10	50	100
Chloroethane		0.5	1	2	5	10	50	100
Trichlorofluoromethane		0.5	1	2	5	10	50	100
1,1-Dichloroethene		0.5	1	2	5	10	50	100
Acetone	1	2.5	5	10	25	50	250	500
Iodomethane	1	2.5	5	10	25	50	250	500
Carbon disulfide	1	2.5	5	10	25	50	250	500
Methylene chloride		0.5	1	2	5	10	50	100
trans-1,2-Dichloroethene		0.5	1	2	5	10	50	100
1,1-Dichloroethane		0.5	1	2	5	10	50	100
Vinyl acetate	1	2.5	5	10	25	50	250	500
cis-1,2-Dichloroethene		0.5	1	2	5	10	50	100
2,2-Dichloropropane		0.5	1	2	5	10	50	100
2-Butanone	1	2.5	5	10	25	50	250	500
Bromochloromethane		0.5	1	2	5	10	50	100
Chloroform		0.5	1	2	5	10	50	100
1,1,1-Trichloroethane		0.5	1	2	5	10	50	100
1,1-Dichloropropene		0.5	1	2	5	10	50	100
Carbon tetrachloride		0.5	1	2	5	10	50	100
Benzene		0.5	1	2	5	10	50	100
1,2-Dichloroethane		0.5	1	2	5	10	50	100
Trichloroethene		0.5	1	2	5	10	50	100
1,2-Dichloropropane		0.5	1	2	5	10	50	100
Dibromomethane		0.5	1	2	5	10	50	100
Bromodichloromethane		0.5	1	2	5	10	50	100
cis-1,3-Dichloropropene		0.5	1	2	5	10	50	100
tert-Butylmethylether		0.5	1	2	5	10	50	100
Chlorobenzene-d5 (IS)								
Toluene-d8 (surr)		0.5	1	2	5	10	50	100
4-Methyl-2-pentanone	1	2.5	5	10	25	50	250	500
Toluene		0.5	1	2	5	10	50	100
trans-1,3-Dichloropropene		0.5	1	2	5	10	50	100
1,1,2-Trichloroethane		0.5	1	2	5	10	50	100
Tetrachloroethene		0.5	1	2	5	10	50	100
1,3-Dichloropropane		0.5	1	2	5	10	50	100
2-Hexanone	1	2.5	5	10	25	50	250	500
Dibromochloromethane		0.5	1	2	5	10	50	100
1,2-Dibromoethane		0.5	1	2	5	10	50	100
Chlorobenzene		0.5	1	2	5	10	50	100
1,1,1,2-Tetrachloroethane		0.5	1	2	5	10	50	100
Ethylbenzene		0.5	1	2	5	10	50	100
m,p-Xylene		1	2	4	10	20	100	200

o-Xylene		0.5	1	2	5	10	50	100
Stryene		0.5	1	2	5	10	50	100
1,4-Dichlorobenzene-d4 (IS)								
Bromofluorobenzene (surr)		0.5	1	2	5	10	50	100
Bromoform		0.5	1	2	5	10	50	100
Isopropylbenzene		0.5	1	2	5	10	50	100
1,1,2,2-Tetrachloroethane		0.5	1	2	5	10	50	100
Bromobenzene		0.5	1	2	5	10	50	100
1,2,3-Trichloropropane		0.5	1	2	5	10	50	100
n-Propylbenzene		0.5	1	2	5	10	50	100
2-Chlorotoluene		0.5	1	2	5	10	50	100
1,3,5-Trimethylbenzene		0.5	1	2	5	10	50	100
4-Chlorotoluene		0.5	1	2	5	10	50	100
1,2,4-Trimethylbenzene		0.5	1	2	5	10	50	100
sec-Butylbenzene		0.5	1	2	5	10	50	100
1,3-Dichlorobenzene		0.5	1	2	5	10	50	100
tert-Butylbenzene		0.5	1	2	5	10	50	100
Isopropyltoluene		0.5	1	2	5	10	50	100
1,4-Dichlorobenzene		0.5	1	2	5	10	50	100
n-Butylbenzene		0.5	1	2	5	10	50	100
1,2-Dichlorobenzene		0.5	1	2	5	10	50	100
1,2-Dibromo-3-chloropropane		0.5	1	2	5	10	50	100
1,2,4-Trichlorobenzene		0.5	1	2	5	10	50	100
Hexachlorobutadiene		0.5	1	2	5	10	50	100
Naphthalene		0.5	1	2	5	10	50	100
1,2,3-Trichlorobenzene		0.5	1	2	5	10	50	100

* Practical Quantitation Limit for Level 1 and 1a (Level 1 - 8260B low level; Level 1a - EPA 524.2)

# Indicates calibration verification concentration level used

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

THE EXTRACTION OF SEMIVOLATILE AND NONVOLATILE ORGANIC COMPOUNDS FROM SOIL, SLUDGE, AND OTHER MISCELLANEOUS SOLID SAMPLES

(GL-OA-E-010 REVISION 10)

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1.0 STANDARD OPERATING PROCEDURE FOR THE EXTRACTION OF SEMIVOLATILE AND NONVOLATILE ORGANIC COMPOUNDS FROM SOIL, SLUDGE AND OTHER MISCELLANEOUS SOLID SAMPLES

2.0 PURPOSE

To describe the manner in which soil or sludge samples are extracted for EPA SW-846 organic analysis methods 8270C, 8081, 8081A, 8082, 8015A, 8310, Florida Department of Environmental Protection FL-PRO, University of Connecticut CT-ETPH, and Alaska AK102 and AK103.

3.0 DISCUSSION

Analytes listed in the above referenced methods are partitioned from soil or sludge matrices, using sonication extraction. The extract is concentrated using Kuderna-Danish techniques coupled with nitrogen gas blowdown. These techniques prepare the sample such that analytes of interest are in solvent and at concentrations suitable for analysis using gas or liquid chromatography.

4.0 DEFINITIONS

4.1 Blank – Anhydrous sodium sulfate used to determine that no background contaminants are present in the extraction process. For AK102/AK103, Ottawa sand is used.

4.2 Laboratory Control Sample (LCS) – Anhydrous sodium sulfate containing the spiking solution to indicate the process is in control and to indicate accuracy. For AK102/AK103, Ottawa sand is used.

4.3 Laboratory Control Sample Duplicate (LCS DUP) - A duplicate of the LCS to indicate reproducibility and to indicate precision. For AK102/AK103, Ottawa sand is used.

4.4 Matrix spike (MS) - A sample in which BNA spiking solution is added. The recovery of matrix spike compounds indicates the presence or absence of matrix interferences.

4.5 Sample Duplicate - A duplicate of a sample indicating reproducibility.

4.6 Surrogate - A solution added to each sample and quality control sample to monitor the efficiency of the extraction process. It contains compounds similar to those being analyzed. For compounds and concentrations refer to Organic Extraction Working Standards Recipe and Production Log. Surrogate solutions expire six months from date opened or date prepared, whichever comes first. All standards are screened prior to use in extractions.

4.7 Spike - A solution added to the laboratory control samples and matrix spikes that contain compounds defined by the referenced method. For compounds and concentrations refer to Organic Extraction Working Standards Recipe and Production Log. The spiking solutions expire six months from date opened or date prepared, whichever comes first. All standards are screened prior to use in extractions.

5.0 SAFETY, HEALTH, AND ENVIRONMENTAL HAZARDS

WARNING

METHYLENE CHLORIDE IS A POSSIBLE CARCINOGEN.
HEXANE IS FLAMMABLE AND TOXIC.

CARDON DISULFIDE IS TOXIC.

ACETONITRILE IS FLAMMABLE AND TOXIC.

ACETONE IS HIGHLY FLAMMABLE.

WARNING

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

5.1 Wear eye protection with side shields while working in the laboratory.

5.2 All chemicals and samples should be treated as a potential health hazard and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client sample MSDSs are also maintained.

5.3 Personal protective equipment

5.3.1 Gloves are required when working with solvents, standards and samples. Solvents, along with any solute in them, can absorb easily through the skin.

5.3.2 Work under a hood when using concentrated acids.

5.3.3 To protect clothes and skin from corrosive material, wear a lab coat.

5.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

5.4.1 Wear a dosimeter at all times while working in the lab to monitor radioactive exposure.

5.4.2 Wear a plastic apron over lab coat when working with radioactive samples.

5.4.3 Protect counter tops with counter paper or work from radioactive sample handling trays.

5.4.4 Prohibit admittance to immediate work area.

5.4.5 Post signs indicating radioactive samples are in the area.

5.4.6 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

5.4.7 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

5.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

5.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

5.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

5.6 Snyder columns may shoot off due to pressure inside the K-D.

5.7 In the event of an accident or medical emergency call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

5.8 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

6.0 APPARATUS AND MATERIALS

(Unless otherwise indicated, all apparatus and materials are suggested only.)

6.1 Glassware

6.1.1 4-oz. amber glass wide mouth jars with Teflon-lined screw caps.

6.1.2 Concentrator tube. Kuderna-Danish 10-mL graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

6.1.3 Evaporative flask, Kuderna-Danish 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.1.4 Snyder column, Kuderna-Danish three ball macro (Kontes K-503000-0121 or equivalent). Rotary evaporation set-up may be used alternatively.

6.1.5 Two mL glass vials with Teflon-lined cap (autosampler vials).

6.1.6 Disposable pipettes: Pasteur.

6.1.7 Glass or Teflon funnels.

6.1.8 200 or 400 mL beaker

6.2 Boiling chips – Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

6.3 Water bath – Heated with concentric ring cover, capable of temperature control ±2°C). The bath should be used in a hood.

6.4 An analytical balance capable of accurately weighting 0.0001 g should be used for preparing standards and percent moisture determination. A top-loading balance capable of weighing to the nearest 0.01 g should be used for sample preparation.

6.5 Stainless steel spatula.

6.6 Sonication.

6.6.1 Ultrasonic cell disrupter: A horn-type sonicator equipped with a titanium tip should be used. A Heat Systems-Ultrasonics, Inc., Model W-385 (475 watt) sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2inch Tapped Disrupter Horn) plus No. 2073/4inch Tapped Disrupter Horn, and No. 419 1/8 inch Standard tapered Microtip probe.

6.6.2 A Sonabox or equivalent is recommended with the above disrupter for decreasing sound (Heat Systems-Ultrasonics, Inc., Model 432 13 or equivalent).

6.7 Nitrogen evaporator with high purity (grade 4.5 or equivalent) nitrogen gas source.

6.8 TurboVap

6.9 TurboVap Concentrator Tubes

7.0 PROCEDURES

7.1 Sample Handling and Preservation:

7.1.1 Sample containers are glass or Teflon with a Teflon lined screw cap. Plastic containers are not used to prevent phthalate or hydrocarbon contamination.

7.1.2 Protect sample containers from light. Some analytes are light sensitive.

7.1.3 Samples will be maintained at 4° ±2°C until extraction begins.

7.1.4 Samples must be extracted within fourteen days from collection.

7.1.5 If samples are not in appropriate containers or holding time has expired, initiate an NCR. For instructions, refer to GL-QS-E-004 for "Documentation of Nonconformance Reporting and Dispositioning, and Control of Nonconforming Items."

7.2 Reagents must meet ACS Analytical criteria. Reagents will not be stored in plastic containers.

7.2.1 Solvents will be screened prior to use.

7.2.1.1 Methylene Chloride (CH_2CL_2) - Pesticide quality or equivalent

7.2.1.2 Acetone (CH_3COCH_3) - Pesticide quality or equivalent

7.2.1.3 Hexane (C_6H_{14}) - Pesticide quality or equivalent

7.2.1.4 Acetonitrile (CH_3CN) - Pesticide quality or equivalent

7.2.2 1:1 Methylene Chloride/Acetone - add 1000 mL Methylene Chloride to 1000 mL of Acetone in 2000 mL tilt.

7.2.3 Anhydrous sodium sulfate (Na_2SO_4) - muffle granular and powder Na_2SO_4 at 400°C for 4 hours; rinse granular Na_2SO_4 with CH_2CL_2 prior to use.

7.2.4 Glass wool - rinse with extraction solvent prior to use.

7.2.5 Ottawa sand.

7.3 Set Up

7.3.1 All batches (up to 20 samples) will be extracted with a blank, LCS, LCS DUP, MS, and a DUP or MSD.

7.3.2 Rinse all glassware with (CH_2CL_2). Label glassware with sample number.

7.3.3 Decant and discard water layer. For AK102 and AK103 samples - Note what percent of the sample the water represents and, if sufficient volume exists, extract and analyze the water for DRO. Also note the apparent condition of the sample (presence of foreign materials, variable particle size, presence of oil sheen, multiple phases, etc.). Homogenize sample. Discard sticks, leaves, rocks, etc.

NOTE: It is assumed that material within the sample container is considered "the sample." Removal of any extraneous material (twigs, leaves, large rocks, etc.) must be documented in the case narrative and bench logbooks.

7.3.4 To avoid loss of more volatile compounds, rapidly weigh 30 g of sample into 200 or 400 mL beaker. Record to nearest 0.1 g.

7.3.4.1 For Paint chip analysis for PCBs, weigh 1.0 g of sample. Record to the nearest 0.1 g. Proceed to Section 7.3.6.

7.3.4.2 For swipe analysis, calculations are determined per swipe. Extract the entire swipe. Proceed to Section 7.3.6.

7.3.5 Add anhydrous sodium sulfate (Na_2SO_4) powder and mix well (up to 60 g can be added) to obtain free-flowing sample.

NOTE: Specific clients (i.e., Navy) require step 7.3.6 to precede this step.

7.3.6 Add 1 mL appropriate surrogate to all samples and quality control samples. Add 1 mL appropriate spiking solution to quality control samples to be spiked. For appropriate surrogate and spiking solution, refer to Appendix 1.

7.3.7 Immediately add appropriate extraction solvent. For extraction solvent, refer to Appendix 1. Solvent is added to cover sample allowing the sonicator probe tip to be approximately 1 inch below the surface without touching the sediment.

7.4 Extraction

7.4.1 Place in properly tuned ultrasonic extractor with tip of 3/4" probe about 1 inch below surface. Sonicate for three minutes with 50% duty cycle and output control set at 8.

7.4.2 Decant and filter extracts through Whatman No. 41, or equivalent filter paper, using vacuum flask with Buchner funnel and rubber stopper.

7.4.3 Repeat three minute sonication twice more with appropriate solvent. Final sonication: pour entire sample into funnel and rinse with extraction solvent. Use vacuum.

7.4.4 Pour sample through solvent rinsed drying funnel containing glass wool and granular Na_2SO_4 into Kuderna-Danish (K-D) with 10 mL concentrator tube for TPH, FL-PRO, CT-ETPH, and AK102/AK103. For BNA, PCB and Pesticides, pour the extract into a turbo-vap tube to be concentrated using the turbo-vaps. Quantitatively wash the extraction flask and drying funnel with 20 - 30 mL extraction solvent. Add these rinses to the K-D.

7.5 Concentration and Packaging

CAUTION

ANALYTES OF INTEREST MAY BE LOST IF SAMPLES ARE CONCENTRATED TOO LOW.

7.5.1 For TPH, FL-PRO, CT-ETPH and AK102/AK103, add a boiling stone and attach 3-ball Snyder column to K-D. Pre-wet column with 1 - 2 mL CH_2Cl_2 for safety and place on 80° - 90°C water bath. (At proper distillation rate, balls will chatter, but chambers will not flood.)

7.5.2 At approximately 5 mL, remove from water bath and allow to cool.

7.5.3 For BNA, concentrate sample to 1 mL. For PCB and Pesticides, concentrate to 5 mL in turbo-vap tube and proceed to step 6.5.4.

CAUTION

ANALYTES OF INTEREST MAY BE LOST IF SOLVENT IS NOT MIXED PROPERLY AND PRESSURE FORCES SOLVENT THROUGH TOP OF SNYDER COLUMN.

7.5.4 Refer to Appendix 1 to determine if solvent exchange is required. If solvent exchange is required, add approximately 50 mL solvent, rinsing down sides of turbo-vap tubes. Concentrate to final volume of 1 mL.

7.5.5 For TPH, FL-PRO, CT-ETPH and AK102/AK103, carefully dry the outside of glassware around concentrator tube/K-D joint to prevent water from contaminating the extract. Remove snyder column and K-D.

7.5.6 Prepare Nitrogen (N_2) Evaporator (N-Evap) for samples by rinsing needles with final solvent to prevent contamination from previous samples. Place concentrator tube on N-Evap with water temperature about 35°C.

CAUTION

ANALYTES OF INTEREST MAY BE LOST IF SAMPLES ARE CONCENTRATED TOO LOW OR TOO FAST.

7.5.7 Use a gentle stream of N_2 concentrate just below desired final volume and reconstitute with final solvent. If solvent exchange was necessary, concentrate to approximately half of desired final volume and then reconstitute with final solvent.

7.5.8 Proceed with clean up if necessary. Concentrate extract using K-D and/or N_2.

7.5.9 Transfer to 2 or 4 mL amber vial with Teflon-lined screw cap. Record final volume. Label with LIMS generated barcoded label. Mark the meniscus. All extracts with the exception of those to be analyzed using AK102 and AK103 should be store at 4° ±2°C. The AK102 and AK103 extracts should be stored in a frost-free freezer at <-10°C.

7.5.10 Rinse glassware with last solvent used before having glassware washed.

8.0 RECORDS MANAGEMENT

8.1 Documentation of Training

8.1.1 Extraction technicians must be properly trained to perform the contents of this SOP. Personnel will extract four laboratory control samples for each analytical SOP referenced within this SOP as training commences. Training is documented per GL-HR-E-003 for Maintaining Technical Training Records.

8.2 Documentation of Extraction

8.2.1 Complete Sample Tracker Form and Data Review Sheet (Appendix 3). Record initial weight of sample, final volume of extract, amount of surrogate and spikes added, and any comments about the extraction process.

Also record all reagent lot numbers like surrogate, spike and solvent lot numbers. (See Appendix 2.) Also note any deviations from this standard operating procedure in the comment section.

8.2.2 Enter initial weight and final volume of each sample into the Laboratory Information Management System (LIMS) and print a hard copy.

8.2.3 Have batch peer reviewed using data review sheet. Note all discrepancies about sample handling and preservation.

8.2.4 These documents are stored in ascending order by batch number in a current notebook. When the current notebook is full, usually two weeks time, the documents are bound and stored. Typically, every three or four months, the bound documents are boxed and relocated to the document storage area.

8.3 Documentation of Standards

Refer to "Laboratory Standards Documentation" (GL-LB-E-007) and "Control of Laboratory Standards" (GL-LB-E-015).

8.0 REFERENCES

9.1 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1B, SW-846, 3rd Edition, Nov. 1986. Method 3550A, "Ultrasonic Extraction," Rev 1, Sept. 1994. USEPA, Washington, D.C. 20460.

9.2 Florida Department of Environmental Protection "Method for Determination of Petroleum Range Organics (Method # FL-PRO).

9.3 Analysis of Extractable Total Petroleum Hydrocarbons (ETPH) using Methylene Chloride, Gas Chromatograph/Flame Ionization Detection, Environmental Research Institute, University of Connecticut, March 1999.

9.4 Determination of Diesel Range Organics, Alaska Method AK102, Version 3-1-99.

9.5 Determination of Residual Range Organics, Alaska Method AK103, Version 3-1-99.

APPENDIX 1: EXTRACTION CONDITIONS

Extraction Conditions for Various Sonication Analyses

Prep	Analysis	Surrogate/Spike[a]	Extraction solvent	Solvent exchange	Clean up
BNA	8270 B	BNA Surrogate/ BNA Spike	1:1 CH_2Cl_2:Acetone	None	None
Pesticide/ PCB[b]	8081 8081A	Pesticide Surrogate/ Pesticide Spike	1:1 CH_2Cl_2:Acetone	Hexane	Florisil
PCB	8082	PCB Soil Surrogate/ PCB Soil Spike	1:1 CH_2Cl_2:Acetone	Hexane	$KMnO_4$/ H_2SO_4
TPH	8015 B	TPH Surrogate/ TPH Spike	CH_2Cl_2	None	None
PAH	8310	PAH Surrogate/ PAH Spike	1:1 CH_2Cl_2:Acetone	Acetonitrile	None
FL-PRO/CT-ETPH	TPH	FL-PRO surrogate FL-PRO Spike	Ch_2Cl_2	None	Silica Gel
AK102 AK103	TPH	AK102/AK103 surrogate AK102/AK103 DRO/RRO LCS	Ch_2Cl_2	None	None

a: Other spiking compounds may be used if client requests non-regulated compounds.

b: GEL has defined Method 8081 into two classes: Pesticides and Pesticides/PCBs. When a batch consists of samples for which Pesticides and/or Pesticides/PCBs are requested, use Pesticide Surrogate and Pesticide Spike.

c: All spikes and surrogates are stored at 4° ±2°C except AK102 and AK103 surrogates and spikes. These standards should be stored at -10° to -20°C.

NOTE: For recipes, concentrations, analytes and diluents generally used, refer to the current Standards Logbook in the Organic Prep Extraction Laboratory.

APPENDIX 2: DATA REVIEW CHECKLIST

DATA REVIEW CHECKLIST FOR EXTRACTABLE ORGANICS

QUALITY CRITERIA	YES	NO	COMMENTS
1. Verify that samples have been extracted within hold time.			
2. Verify that samples and QC on sample tracker correspond to batch sheet.			
3. Verify that surrogate, spike, and solvents have been recorded on sample tracker.			
4. If batch is BNA, did sample change color when acid and/or base was added.(Pink or Yellow)			
5. Verify that there is a vial for every extract listed on the tracker.			
6. Verify that the meniscus is marked on every vial.			
7. Verify the vials are barcoded to ensure traceability.			
8. Verify that surrogate and spike checks were were made.(witness the addition of)			
9. Verify paperwork is legible. Strike overs are initialed and dated.			
10. Verify lims data report with the written tracker for errors.			
11. Verify that temperature monitoring was done. according to SOP#GL-LB-E-004.			
12. Verify that no error messages were received while entering standards into database.			
REVIEWERS SIGNATURE			
ANALYST	DATE		
PEER/GROUP LEADER	DATE		

APPENDIX 3: EXTRACTION TRACKER FORM

Prep #	Solvent Lots	CH2Cl2	Cleanup or Derivation Techniques	Sulfur Lot:	GEL SOP Reference	Rev#
Date:	Hexane:	Toluene:	GPC bead Lot:	Florisil Lot:	GL-OA-E-	
Matrix W S Other	Acetone:	Isooctane:	Silica gel Lot:	Acid Lot:	GL-OA-E-	
Prep Method:	Ether:	Methanol:	Alumina Lot:		GL-OA-E-	
					GL-OA-E-	
Surrogate Std. Sol. ID:		Conc.	Vol. Added (mL):		GL-OA-E-	
MB/LCS Std. Sol. ID:		Conc.	Vol. Added (mL):		GL-OA-E-	

Client	GEL Sample ID #	Date Extracted	Sample Wt (g) or Vol (mL)	Sample pH			Extract Analyst	Spikes Verified By	Cleanup (clnup) Applied or Derivation	Volumes of Extract (mL)				Final Solv	Date Cleaned or Deriv & Initials	Re-ext smpl X	Comments (Include SDG# when applicable)
				Int	Int Ext	Sec Ext				Prior to Clnup	Amt Cleaned	After Clnup	Final Ext Vol				
MS																	
MSD																	
Method Blank																	
LCS #1																	
LCS #2																	

SOPs-OA/OrgExtTracker
Rev 2 Effective 8/00

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

EXTRACTION OF SEMIVOLATILE AND NONVOLATILE ORGANIC COMPOUNDS FROM GROUNDWATER, WASTEWATER, AND OTHER AQUEOUS SAMPLES

(GL-OA-E-013 REVISION 12)

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR THE EXTRACTION OF SEMIVOLATILE AND NONVOLATILE ORGANIC COMPOUNDS FROM GROUNDWATER, WASTEWATER AND OTHER AQUEOUS SAMPLES

2.0 PURPOSE

To describe the manner in which groundwater, wastewater, and other aqueous samples are extracted for organic analysis methods 8270C, 8081, 8081A, 8082, 8015A, 8015B, 8310, 625, 608, Florida Department of Environmental Protection FL-PRO, Alaska AK102, and Environmental Research Institute University of Connecticut CT-ETPH.

3.0 DISCUSSION

Analytes listed in the above referenced methods are partitioned from water matrices using separatory funnels for a liquid/liquid extraction. The extract is concentrated using Kuderna-Danish techniques coupled with nitrogen gas blowdown. These techniques prepare the sample such that analytes of interest are in solvent and at concentrations suitable for analysis using gas or liquid chromatography.

4.0 DEFINITIONS

4.1 Blank - Organic free reagent water used to determine that no background contaminants are present in the extraction process.

4.2 Laboratory Control Sample (LCS) - Organic free reagent water containing the spiking solution to indicate the process is in control and to indicate accuracy.

4.3 Laboratory Control Sample Duplicate (LCS DUP) - A duplicate of the LCS to indicate reproducibility and to indicate precision.

4.4 Matrix spike - A sample in which the spiking solution is added. The recovery of matrix spike compounds indicates the presence or absence of matrix interferences. This may be duplicated (MSD) at a client's request and if enough sample is provided.

4.5 Sample Duplicate - A duplicate of a sample indicating reproducibility.

4.6 Surrogate - A solution added to each sample and quality control sample to monitor the efficiency of the extraction process. It contains compounds similar to those being analyzed. For compounds and concentrations refer to the Create/Edit/View Reference Materials section of ALPHA LIMS. Surrogate solutions expire six months from date opened or date prepared, whichever comes first. All standards are screened prior to use in extractions.

4.7 Spike - A solution added to the laboratory control samples and matrix spikes that contain compounds defined by the referenced method. For compounds and concentrations, refer to the Create/Edit/View Reference Materials section of ALPHA LIMS. The spiking solutions expire six months from date opened or date prepared, whichever comes first. All standards are screened prior to use in extractions.

5.0 SAFETY, HEALTH AND ENVIRONMENTAL HAZARDS

WARNING

METHYLENE CHLORIDE IS A POSSIBLE CARCINOGEN. HEXANE IS FLAMMABLE AND TOXIC. ACETONITRILE IS FLAMMABLE AND TOXIC.

SODIUM HYDROXIDE CAUSES SEVERE BURNS AND MAY BE FATAL IF SWALLOWED.

CARBON DISULFIDE IS TOXIC.

SULFURIC ACID IS CORROSIVE, CAUSES SERIOUS BURNS AND MAY BE FATAL IF SWALLOWED.

WARNING

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

5.1 Wear eye protection with side shields while working in the laboratory.

5.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDS forms are maintained in the laboratory.

5.3 Personal protective equipment

5.3.1 Gloves are required when working with solvents, standards and samples. Solvents, and any solute in them, can absorb easily through the skin.

5.3.2 Work under a hood when using concentrated acids.

5.3.3 To protect clothes and skin from being exposed to corrosive material, wear a lab coat.

5.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

5.4.1 Wear a dosimeter at all times while working in the lab to monitor radioactive exposure.

5.4.2 Wear a lab coat when working with radioactive samples.

5.4.3 Protect counter tops with counter paper or work from radioactive sample handling trays.

5.4.4 Prohibit admittance to immediate work area.

5.4.5 Post signs indicating radioactive samples are in the area.

5.4.6 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

5.4.7 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

5.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

5.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

5.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

5.6 Solvent in a closed separatory funnel creates excessive pressure, so always vent immediately when beginning to shake.

5.7 When venting a separatory funnel, point stopcock end toward fume hood and always away from other people working in the area to minimize solvent fumes.

5.8 Hood doors should be pulled down partially while K-D apparatus are on the bath. Snyder columns may shoot off due to pressure inside the K-D.

5.9 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

5.10 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

6.0 APPARATUS AND MATERIALS

(Unless otherwise indicated, all apparatus and materials are suggested only.)

6.3 Glassware

6.3.1 Separatory funnel – 2000-mL with Teflon stopcock or equivalent.

6.3.2 Concentrator tube. Kuderna-Danish 10-mL graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test.

6.3.3 Evaporative flask, Kuderna-Danish 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with clips.

6.3.4 Snyder column, Kuderna-Danish three ball macro (Kontes K-503000-0121 or equivalent). Rotary evaporation set-up may be used alternatively.

6.3.5 Two mL glass vials with Teflon-lined cap (autosampler vials).

6.3.6 Disposable pipettes: Pasteur.

6.3.7 Graduated cylinders: 250-mL.

6.3.8 Glass or Teflon funnels.

6.4 Boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

6.5 Water bath - Heated with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

6.6 Nitrogen evaporator with high purity (grade 4.5 or equivalent) nitrogen gas source.

7.0 PROCEDURES

7.1 Sample Handling and Preservation

7.1.1 Sample containers should be glass or Teflon with a Teflon lined screw cap. Plastic containers must not be used to prevent phthalate or hydrocarbon contamination.

7.1.2 Sample containers should be protected from light, for some analytes are light sensitive.

7.1.3 Samples are to be maintained at 4°C ±2 until extraction begins.

7.1.4 Samples must be extracted within seven days from collection.

7.1.5 If samples are not in appropriate containers or holding time has expired, write an NCR. For instruction on writing an NCR, refer to "Documentation of Nonconformance Reporting and Dispositioning, and Control of Nonconforming Items" (GL-QS-E-004).

7.2 Reagents: Reagents should meet ACS Analytical criteria. Reagents should not be stored in plastic containers.

7.2.1 Solvents - should be screened prior to use

7.2.1.1 Methylene Chloride (CH_2Cl_2) - Pesticide quality or equivalent
7.2.1.2 Acetone (CH_3COCH_3) - Pesticide quality or equivalent
7.2.1.3 Hexane (C_6H_{14}) - Pesticide quality or equivalent
7.2.1.4 Acetonitrile (CH_3CN) - Pesticide quality or equivalent

7.2.2 1:1 Sulfuric acid (H_2SO_4) - slowly add 100 mL sulfuric acid to 100 mL of organic free reagent water in Erlenmeyer flask

7.2.3 10 N Sodium Hydroxide - dissolve 40 g NaOH in organic free reagent water and dilute to 100 mL

7.2.4 Anhydrous sodium sulfate (Na_2SO_4) - muffle granular Na_2SO_4 at 400°C for 4 hours and rinse with extraction solvent prior to use

7.2.5 Glass wool - rinse with extraction solvent prior to use

7.3 Set Up

7.3.1 All batches (up to 20 samples) are extracted with a minimum of quality control samples including blank, LCS, MS, MSD or duplicate.

7.3.2 Rinse all glassware with Methylene chloride (CH_2Cl_2). Label glassware with sample number.

7.3.3 Mark meniscus on sample bottle for eventual volume determination.

7.3.4 Check pH and record.

NOTE: All pH measurements require the use of a pre-rinsed, 1 mL serological glass pipet to deliver a small aliquot of sample to a wide-range pH indicator strip.

7.3.5 Transfer sample to separatory funnel.

7.3.6 Add appropriate surrogate to all samples and quality control samples. Add appropriate spiking solution to quality control samples to be spiked. For appropriate surrogate and spiking solution, refer to Appendix 1. For volume of surrogate and spike added, refer to Appendix 2.

7.3.7 Adjust pH to extraction range. (See Appendix 1.)

7.3.8 Add 60 mL of CH_2Cl_2 to sample container to rinse. Transfer to separatory funnel.

7.4 Extraction **WARNING**

METHYLENE CHLORIDE CREATES EXCESSIVE PRESSURE VERY RAPIDLY, POSSIBLY CAUSING SEPARATORY FUNNEL TO EXPLODE.

7.4.1 Shake vigorously for one to two minutes. Vent often. Allow layers to separate. If emulsion interface between layers is more than 1/3 size of solvent layer, employ one of the following mechanical techniques to break emulsion: stirring, quantitative filtration through glass wool, centrifugation, or other physical procedures.

7.4.2 Drain CH_2Cl_2 layer through pre-rinsed thistle funnel containing prepped glass wool and muffled anhydrous sodium sulfate (Na_2SO_4) into a K-D with 10 mL concentrator tube.

7.4.3 Add 60 mL of CH_2Cl_2 and repeat steps 6.4.3 through 6.4.4 for a total of three extractions using the appropriate volume of CH_2Cl_2.

7.4.4 Adjust pH if additional extractions are required and repeat steps 6.4.1 through 6.4.3. Refer to Appendix 1 for pH adjustment criteria.

7.4.5 Rinse thistle funnel with 20 - 30 mL CH_2Cl_2. Add this rinse to the K-D.

7.4.6 Measure initial volume by filling sample container to marked meniscus. Transfer contents to 1 liter graduated cylinder and record volume to nearest 5 mL.

NOTE: The use of a solvent-rinsed graduated cylinder is required by specific clients (i.e. Navy).

7.5 Concentration and Packaging

CAUTION

ANALYTES OF INTEREST MAY BE LOST IF SAMPLES ARE CONCENTRATED TOO LOW.

7.5.1 Add small prepped boiling chip and Snyder column to K-D. Pre-wet column with 1 - 2 mL CH_2Cl_2 for safety and place on 80 - 90°C water bath. (At proper distillation rate, balls will chatter, but chambers will not flood.)

7.5.2 At approximately 5 mL, remove from water bath and allow to cool.

CAUTION

ANALYTES OF INTEREST MAY BE LOST IF SOLVENT IS NOT MIXED PROPERLY AND PRESSURE FORCES SOLVENT THROUGH TOP OF SNYDER COLUMN.

7.5.3 Refer to Appendix 1 to determine if solvent exchange is required. If solvent exchange is required, add solvent through Snyder column until approximately 10 mL of solvent is in concentrator tube. Mix in large part of K-D. Return to bath for 30 minutes or until solvent volume has concentrated to approximately 1 mL. Remove from bath, rinse Snyder column with small amount of solvent, and allow to cool.

7.5.4 For FL-PRO TPH/CT-ETPH analysis, proceed with the silica gel cleanup procedure (See GL-OA-E-049). Since solvent exchange is not required, the extract is then concentrated using the N-Evap to 1.0 mL, and then brought to a final volume of 2.0 mL with carbon disulfide.

7.5.5 Carefully dry the outside of glassware around concentrator tube/K-D joint to prevent water from contaminating the extract. Remove snyder column and K-D. Be sure to label concentrator tube with sample number.

7.5.6 Prepare Nitrogen (N_2) Evaporator (N-Evap) for samples by rinsing needles with final solvent to prevent contamination from previous samples. Place concentrator tube on N-Evap with water temperature about 35°C. Do not adjust flow rate of needle, only of the entire unit.

CAUTION

ANALYTES OF INTEREST MAY BE LOST IF SAMPLES ARE CONCENTRATED TOO LOW OR TOO FAST.

7.5.7 Using a gentle stream of N_2 concentrate just below (not below 0.3 mL) desired final volume and reconstitute with final solvent. If solvent exchange was necessary, concentrate to approximately 1 mL, reconstitute with final solvent to 2 mL, and then concentrate to desired final volume.

7.5.8 Proceed with clean up if necessary. See Appendix 1 for appropriate clean up.

7.5.9 Using GENTLE stream of N_2 concentrate to appropriate volume.

7.5.10 Transfer to 2 or 4 mL amber vial with Teflon-lined screw cap using a 1 mL syringe. Record final volume. Label with LIMS generated barcoded label. Mark the meniscus. Store at 4° ±2°C. For Alaska DRO, store at -10° C or colder.

7.5.11 Rinse glassware with ChemSolve solution before having glassware washed.

8.0 RECORDS MANAGEMENT

8.1 Documentation of Training

8.1.1 Extraction technicians must be properly trained to perform the contents of this SOP. Personnel must extract four laboratory control samples for each analytical SOP referenced within this SOP as training commences. Training documentation is maintained per "Employee Training" (GL-HR-E-002).

8.1.2 LCS/LCS DUP demonstrates on a continuing basis that personnel are properly trained.

8.2 Documentation of Extraction

8.2.1 Complete sample tracker form and Data Review Sheet (Appendix 3). Record initial volume of sample, final volume of extract, amount of surrogate and spikes added, the concentration of surrogate and spiking solutions, and any comments about the extraction process. Also record all reagent lot numbers like surrogate, spike and solvent lot numbers. (See Appendix 4.) Also note any deviations from this standard operating procedure in the comment section.

8.2.2 Enter initial and final volume of each sample into the Laboratory Information Management System (LIMS) and print a hard copy.

8.2.3 These documents are stored in ascending order by batch number in a current notebook. When the current notebook is full, usually two weeks time, the documents are bound and stored. Typically, every three or four months, the bound documents are disposed. A copy is maintained with the analytical data.

8.3 Documentation of Standards

8.3.1 Refer to the following SOPs for standards documentation:

8.3.1.1 "Laboratory Standards Documentation" (GL-LB-E-007)
8.3.1.2 "Control of Laboratory Standards" (GL-LB-E-015).

9.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

10.0 REFERENCES

10.1 Test Methods for Evaluating Solid Waste: Laboratory Manual: Physical/ Chemical Methods, Volume 1B, SW-846, Third Edition, November 1986. Method 3510C, "Separatory Funnel Liquid-Liquid Extraction," Revision 3, December 1996.

10.2 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act: Final Rule and Interim Final Rule and Proposed Rule, Friday, October 26, 1984, Methods 625 and 608.

10.3 Florida Department of Environmental Protection "Method for Determination of Petroleum Range Organics (Method # FL-PRO).

10.4 Analysis of Extractable Total Petroleum Hydrocarbons (ETPH) using Methylene Chloride, Gas Chromatograph/Flame Ionization Detection, Environmental Research Institute, University of Connecticut, March 1999.

10.5 Method AK 102, "Determination of Diesel Range Organics," Version 3-1-99.

APPENDIX 1: EXTRACTION CONDITIONS

Extraction Conditions for Various Water Analyses

Prep	Analysis	Surrogate/Spike[a]	Extraction pH	pH Change	Solvent Exchange	Clean up Required
BNA	8270 C	BNA Surrogate/ BNA Spike	<2	>11	None	
Pesticide/ PCB[c]	8081 8081A	Pesticide Surrogate/ Pesticide Spike	5 - 9	None	Hexane	Florisil
PCB	8081 8082	PCB H_2O Surrogate/ PCB H_2O Spike	5 - 9	None	Hexane	KM_nO_4/ H_2SO_4
TPH	8015 A 8015 B	TPH Surrogate/ TPH Spike	<2	None	None	
PAH	8310	PAH Surrogate/ PAH Spike	5 - 9	None	Acetonitrile	
BNA	625	BNA Surrogate/ 625 Spike	<2	>11	None	
Pesticide/ PCB	608	Pesticide Surrogate/ 608 Spike	5 - 9	None	Hexane	Florisil
PCB	608	PCB H_2O Surrogate/ PCB H_2O Spike	5 - 9	None	Hexane	KM_nO_4/ H_2SO_4
BNA	TCLP	BNA Surrogate/TCLP BNA Spike	<2	>11	None	
Pesticide[b]	TCLP	Pesticide Surrogate/TCLP Pesticide Spike/ Toxaphene/ Chlordane	5 - 9	None	Hexane	
FL-PRO/CT-ETPH	TPH	FL-PRO Surrogate FL-PRO Spike	<2[d]	None	None	Silica Gel
AK102	TPH	TPH Surrogate AK102 Spike	<2[d]	None	None	

a: Other spiking compounds may be used if client requests non-regulated compounds.

b: Due to chromatography of pesticide compounds regulated by TCLP, extract separately a TCLP spike, a Toxaphene spike, and a Chlordane spike for each spiked sample.

c: GEL has defined Method 8081 into two classes of compounds: Pesticides and Pesticides/PCBs. When a batch consists of samples requesting Pesticides and/or Pesticides/PCBs, use Pesticide Surrogate and Pesticide Spike.

d: Samples should arrive preserved with either HCl or H_2SO_4 giving a pH of less than 2. If the pH of the sample is greater than 2, do not adjust the pH yourself. Do not acidify the method blank or LCS.

NOTE: For recipes, concentrations, analytes and diluents generally used, refer to the Create/Edit/View Reference Materials section of ALPHA LIMS.

APPENDIX 2: SURROGATE AND SPIKE VOLUMES

Typical Volumes: Initial, Final, Surrogate/Spike, and Solvent

Prep	Analysis	Initial Volume[a]	Final Volume	Surrogate/ Spike Volume
BNA	8270 C	1000 mL	1 mL	1 mL
Pesticide/ PCB	8081 8081A	1000 mL	1 mL	1 mL
PCB	8081 8082	1000 mL	1 mL	1 mL
TPH	8015 A 8015 B	1000 mL	1 mL	1 mL
PAH	8310	1000 mL	1 mL	1 mL
BNA	625	1000 mL	1 mL	1 mL
Pesticide/ PCB	608	1000 mL	1 mL	1 mL
PCB	608	1000 mL	1 mL	1 mL
BNA	TCLP	100 mL	1 mL	1 mL
Pesticide	TCLP	20 mL	1 mL	1 mL
FL-PRO/CT-ETPH	TPH	1000 mL	2 mL[b]	1 mL
AK102	TPH	1000 mL	1 mL	1 mL

a: These volumes are guidelines. Due to nature of sample or amount of sample collected, other volumes may be used if diluted to 1000 mL with organic free water. Surrogate, spikes, and final volumes should be adjusted to maintain reporting limits.

b: Sample extract is concentrated to 1.0 mL in methylene chloride and brought to a final volume of 2.0 mL with carbon disulfide.

c: All spike and surrogate solutions are stored at 4° ±2°C except for Alaska DRO. Alaska DRO standards are stored in a frost-free freezer at -10°C to 120°C.

APPENDIX 3: DATA REVIEW CHECKLIST

QUALITY CRITERIA	YES	NO	COMMENTS
1. Verify that samples have been extracted within hold time.			
2. Verify that samples and QC on sample tracker correspond to batch sheet.			
3. Verify that surrogate, spike, and solvents have been recorded on sample tracker.			
4. If batch is BNA, did sample change color when acid and/or base was added.(Pink or Yellow)			
5. Verify that there is a vial for every extract listed on the tracker.			
6. Verify that the meniscus is marked on every vial.			
7. Verify the vials are barcoded to ensure traceability.			
8. Verify that surrogate and spike checks were were made.(witness the addition of)			
9. Verify paperwork is legible. Strike overs are initialed and dated			
10. Verify lims data report with the written tracker for errors.			
11. Verify that temperature monitoring was done. according to SOP#GL-LB-E-004.			
12. Verify that no error messages were received while entering standards into database.			
REVIEWERS SIGNATURE			
ANALYST	DATE		
PEER/GROUP LEADER	DATE		

APPENDIX 4: SAMPLE TRACKER FORM

Prep #	Solvent Lots	CH2Cl2	Cleanup or Derivation Techniques	Sulfur Lot:	GEL SOP Reference	Rev#
Date:	Hexane:	Toluene:	GPC bead Lot:	Florisil Lot:	GL-OA-E-	
Matrix W S Other	Acetone:	Isooctane:	Silica gel Lot:	Acid Lot:	GL-OA-E-	
Prep Method:	Ether:	Methanol:	Alumina Lot:		GL-OA-E-	
					GL-OA-E-	
Surrogate Std. Sol. ID:		Conc.	Vol. Added (mL):		GL-OA-E-	
MB/LCS Std. Sol. ID:		Conc.	Vol Added (mL)		GL-OA-E-	

Client	GEL Sample ID #	Date Extracted	Sample Wt (g) or Vol (mL)	Sample pH Int Ext	Sample pH Int Ext	Sample pH Sec Ext	Extract Analyst	Spikes Verified By	Cleanup (Group) Applied or Derivatization	Volumes of Extract (mL) Prior to Cleanup	Volumes of Extract (mL) Amt Cleaned	Volumes of Extract (mL) After Cleanup	Volumes of Extract (mL) Final Ext Vol	Final Solv	Date Cleaned or Deriv & Initials	Re-ext sampl X	Comments (Include SDG# when applicable)
MS																	
MSD																	
Method Blank #1																	
LCS #1																	
LCS #2																	

SOPs-OA/OrgExtTracker
Rev 2 Effective 8/00

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

POLYNUCLEAR AROMATIC HYDROCARBONS

(GL-OA-E-030 REVISION 7)

APPLICABLE TO METHODS:
EPA SW-846 Methods 8310 and 8000B

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1.0 STANDARD OPERATING PROCEDURE FOR POLYNUCLEAR AROMATIC HYDROCARBONS

2.0 METHOD CODES

2.1 EPA SW-846 Method 8310

2.2 EPA SW-846 Method 8000B

3.0 METHOD SUMMARY, OBJECTIVE AND PURPOSE

3.1 This is a liquid chromatographic procedure for quantitatively determining certain Polynuclear Aromatic Hydrocarbons. The analytical guidance for the detection and quantitation of the applicable Polynuclear Aromatic Hydrocarbons has been taken from Methods 8310 and 8000B of "Test Methods for Evaluating Solid Waste," EPA Manual SW-846.

3.2 This method applies to ground water, soil, leachates, and miscellaneous matrices. Referenced procedure is 8310 and 8000B of "Test Methods for Evaluating Solid Waste" (EPA Manual SW-846.)

The following compounds can be quantitatively determined by this procedure:

Compound Name	CAS Number
Acenaphthene	83-32-9
Acenaphthylene	206-96-8
Anthracene	120-12-7
Benzo(a)anthracene	56-55-3
Benzo(a)pyrene	50-32-8
Benzo(b)fluoranthene	205-99-2
Benzo(ghi)perylene	191-24-2
Benzo(k)fluoranthene	207-08-9
Chrysene	218-01-9
Dibenzo(a,h)anthracene	53-70-3
Fluoranthene	206-44-0
Fluorene	86-73-7
Indeno(1,2,3-cd)pyrene	193-39-5
Naphthalene	91-20-3
Phenanthrene	85-01-8
Pyrene	129-00-0
1-Methylnaphthalene	90-12-0
2-Methylnaphthalene	91-57-6

3.3 This method provides the High Performance Liquid Chromatographic (HPLC) conditions for detection of trace levels of polynuclear aromatic hydrocarbons. Prior to use of this method, the appropriate sample extraction technique must be used. (See "Extraction of Semivolatile and Nonvolatile Organic Compounds from Soil, Sludge and Other Miscellaneous Samples" (GL-OA-E-010) for solids, and "Extraction of Semivolatile and Nonvolatile Organic Compounds from Groundwater, Wastewater, and Other Aqueous Samples" (GL-OA-E-013) for liquids.) A 20µL aliquot is usually injected into the HPLC system. The sample then passes through the reverse phase column, which performs analyte separation. The separated analytes then pass through the diode array detector (DAD) and fluorescence detector (FLD). Analyte confirmation is performed by the signals from the diode array detector (DAD) and fluorescence detector (FLD). Signal

output is collected and processed initially using Hewlett Packard Chemstation software. Additional data reduction is performed using Thru Put Target software.

4.0 METHOD PERFORMANCE ANALYST VERIFICATION

4.1 See the Group Leader for current MDL studies for liquid and solid matrix MDLs and PQLs.

4.2 Method Precision: See the Group Leader for current SPC limits for RPD and %R.

4.3 LCS and LCS %Recovery: See the Group Leader for current SPC limits for RPD and %R.

4.4 Method Bias: See the Group Leader for current SPC limits for surrogate recovery.

4.5 MS and MSD %Recovery: See the Group Leader for current SPC limits for RPD and %R.

5.0 DEFINITIONS

5.1 HPLC - High performance liquid chromatography

5.2 DAD - Diode array detector

5.3 FLD - Fluorescence detector

5.4 ALPHA LIMS – GEL's laboratory information management system.

5.5 ChemStation - Software package used to control HPLC instruments including data acquisition and temporary storage.

5.6 Calibration Standard (CAL) - A solution prepared from the primary stock solution. The CAL solutions are used to calibrate the instrument.

5.7 Check Standard (CCV/ICV/CVS) - A solution of the method analytes used to evaluate the performance of the instrument with respect to a defined set of criteria. The check standard concentration is at the calibration midpoint and is prepared from a separate source than the calibration standards.

5.8 Matrix Spike (MS) - An aliquot of a known sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed like a sample and its purpose is to evaluate the accuracy of the method.

5.9 Laboratory Control Sample (LCS) - An aliquot of reagent water to which a known quantity of the method analyte is added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine if methodology is in control.

5.10 Method Blank - An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents and reagents which are used with other samples. The method blank is used to determine if method analytes or other interferences are present in the laboratory environment.

5.11 Sample Duplicate (Dup) - A duplicate of a selected sample. The Dup will demonstrate analytical precision.

5.12 TARGET – Data Analysis Software used to process and store analytical data.

6.0 METHOD VARIATION

Referenced procedure requires each organization to develop a method of verifying possible PAH compounds. By using the full spectrum of the DAD, an alternative positive verification is accomplished by comparing the suspect compound spectrum against a compound standard spectrum.

7.0 SAFETY PRECAUTIONS AND WARNINGS

The toxicity/carcinogenicity of various compounds used in this procedure has not been precisely defined. Treat all chemicals as a potential health hazard and limit exposure to them to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals used in this SOP. A reference file of Material Safety Data Sheets (MSDS) is available to all personnel involved in this SOP via GEL's Intranet. If necessary, contact the safety coordinator for specific MSDS sheets.

8.0 INTERFERENCES

8.1 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, under the conditions of the analysis, by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

8.2 Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

8.3 Interferences co-extracted from the sample will vary considerably from source to source. Although a general cleanup technique is provided as part of the method, individual samples may require additional cleanup approaches to achieve the sensitivity required.

8.4 The chromatographic conditions described allow for a unique resolution of the specific PAH compounds covered by this method. Other PAH compounds, in addition to matrix artifacts, may interfere.

9.0 APPARATUS AND MATERIALS; REAGENTS; EQUIPMENT AND INSTRUMENTS

9.1 General Items

- 9.1.1 Microliter syringes
- 9.1.2 2 mL amber vials with Teflon™-lined septa's and screw caps.
- 9.1.3 PTFE filters, 0.45 mm or greater

9.2 Chemicals (Vendors listed subject to change)

- 9.2.1 PAH Performance Check Solution (presently purchased from AccuStandard, Inc.)
- 9.2.2 Acetonitrile HPLC grade or better (presently purchased from VWR)
- 9.2.3 Surrogate Decafluorobiphenyl (presently purchased from Chem Service and O2SI)
- 9.2.4 HPLC grade H2O or better (presently purchased from EM Science)
- 9.2.5 8310 PAH Calibration Standard (presently purchased from O2SI)

9.3 Equipment

- 9.3.1 Presently use a Vydac 250 x 4.6 mm C-18 reverse phase column
- 9.3.2 Gradient pumping system HP model 1100 or equivalent
- 9.3.3 Software capable of average calculations
- 9.3.4 DAD HP model 1100 or equivalent
- 9.3.5 Fluorescence HP model G1321A or equivalent

NOTE: The apparatus listed above is the recommended instrumentation and equipment. This does not list all of the required equipment, but the minimum needed to complete the analysis.

10.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

10.1 Samples must be collected in an amber glass bottle with a Teflon lined cap. The collection container must be washed with acetone and hexane, rinsed, and dried before use in order to minimize contamination.

10.2 Protect samples from light and store as stated in the current revision of "Sample Receipt, Login and Storage" (GL-SR-E-001). All liquid samples have a holding date of seven days from the date of collection to the time of extraction. Once extracted, the extract must be analyzed within forty days. However, during this period of time the extracts are kept refrigerated at 4°±2°C in amber vials with Teflon lined screw caps. When holding dates are missed, the data is flagged by ALPHA LIMS, the analyst and the data reviewer.

10.3 If the sample is outside of the holding time window, notify the applicable group leader or project manager for guidance.

10.4 Sample holding times, also mentioned in Section 6.0 of Method 8310, are as follows:

10.4.1 Liquids are to be extracted within seven (7) days after sample collection.
10.4.2 Solids are to be extracted within fourteen (14) days after sample collection.
10.4.3 All samples are to be analyzed within forty (40) days after extraction.

11.0 SAMPLE PREPARATION TECHNIQUES

Refer to EPA Method 8310, GEL SOPs "Extraction of Semivolatile and Nonvolatile Organic Compounds from Soil, Sludge and Other Miscellaneous Samples" (GL-OA-E-010) for solids, and "Extraction of Semivolatile and Nonvolatile Organic Compounds from Groundwater, Wastewater, and Other Aqueous Samples" (GL-OA-E-013) for liquids.

12.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL STANDARDS

12.1 Standard Solutions

12.1.1 Source Standard Solutions are prepared commercially by AccuStandard, Inc. or other certified suppliers for Polynuclear Aromatic Hydrocarbons. They are stored in a breakseal amber vial or equivalent in the refrigerator at 4°±2°C. They are replaced according to the expiration date designated on the vial by the vendor or in accordance with GL-LB-E-007 for Laboratory Standards Documentation and GL-LB-E-015 for Control of Laboratory Standards.

12.1.2 Calibration Standards are prepared at a minimum of five concentration levels for each compound. It is prepared by diluting the stock solution with acetonitrile. The concentration ranges for the calibration standards are found in the standards log.

See standards log for recipes for making all calibration and quality control samples.

12.2 Calibration Check Standard is a standard from a different source than the calibration standards used to verify that the instrument is calibrated correctly. The reading must be within 85% - 115% of the actual value. The stock for the check standards is prepared by commercial vendors. It is stored in a Teflon-lined screw cap vial at 4°±2°C. The concentrations of the check standards are prepared at the

midpoint of the curve. See the standards log in ALPHA LIMS for current concentrations and recipe for preparing check standards.

12.3 The source standards are received with a certificate of analysis and labeled in accordance with GL-LB-E-007 for Laboratory Standards Documentation. For any intermediate or working standards prepared from one or more source standards, GEL assigns an expiration date to these standards equal to but not exceeding the earliest expiration date of any source standard used to make one of these intermediate or working standards.

12.4 When a standard is prepared, an identification number is assigned to that standard. If another standard is prepared by diluting the first, the diluted standard must be given a unique identification number also.

12.5 All standards are maintained in Refrigerator Number 22.

12.6 The surrogate is prepared at a nominal concentration of 250 ppm. However this may differ based on instrument/sample conditions. Refer to ALPHA LIMS for concentrations and recipes.

12.7 The spiking solution containing some or all of the compounds listed below is prepared with the following nominal concentrations:

Naphthalene	50 ppm
Acenaphthylene	50 ppm
Acenaphthene	50 ppm
Flourene	50 ppm
Phenanthrene	50 ppm
Anthracene	50 ppm
Fluoranthene	5 ppm
Pyrene	5 ppm
Benzo(a)anthracene	5 ppm
Chrysene	5 ppm
Benzo(b)fluoranthene	5 ppm
Benzo(k)fluoranthene	2.5 ppm
Benzo(a)pyrene	5 ppm
Dibenzo(a,h)anthracene	5 ppm
Benzo(g,h,i)perylene	5 ppm
Indeno(1,2,3,-cd)pyrene	5 ppm
1-Methylnaphthalene	50 ppm
2-Methylnaphthalene	50 ppm

However, this may differ based on instrument/sample and dilution requirements. Refer to ALPHA LIMS for nominal concentrations and recipes.

12.8 The surrogate is prepared at a nominal concentration of 250 ppm. However, this may differ based on instrument/sample conditions. See ALPHA LIMS for current concentrations and recipes.

Calibration standards currently being used but not limited to those listed below are:

Ultra Scientific	EPA-2138N
250 Smith Street	EPA-2139N
North Kingstown, RI 02852	RAH-044
	RAH-045
AccuStandard	610-QC

25 Science Park New Haven, CT 06511	610-QC-FL 610-QC-FL-10X
Chem Service 660 Tower Lane P.O. Box 3108 West Chester, PA 19381	G-1160 F-904AS
NSI Environmental Solutions 2 Triangle Drive P.O. Box 12313 Research Triangle Park, NC 27709	1288 0562
O2SI 2040 Savage Road Charleston, SC 29407	110092-01

12.8.1 The current calibration standards are made from O2SI (110092-01) and the appropriate solvent. (Refer to ALPHA LIMS for current recipes).

Analyte concentrations are listed in the following table:

TABLE 1
CALIBRATION STANDARDS

Analyte (µg/mL)	Ultra EPA-2138N	Ultra EPA-2139N	Accustandard 610-QC	Accustandard 610-QC-FL	O2SI 110092-01
Decafluorobiphenyl	-	-	-	-	5000
Naphthalene	1000	-	1000	1000	1000
Acenaphthylene	-	1000	1000	1000	1000
Acenaphthene	1000	-	1000	1000	1000
Fluorene	1000	-	1000	1000	1000
Phenanthrene	-	1000	1000	1000	1000
Anthracene	1000	-	1000	1000	1000
Fluoranthene	-	100	100	100	100
Pyrene	100	-	100	100	100
Benzo(a)anthracene	-	100	100	100	100
Chrysene	100	-	100	100	100
Benzo(b)fluoranthene	-	100	100	100	100
Benzo(k)fluoranthene	50	-	50	50	50
Benzo(a)pyrene	-	100	100	100	100
Dibenzo(a,h)anthracene	-	100	100	100	100
Benzo(g,h,i)perylene	-	100	100	100	100
Indeno(1,2,3-cd)pyrene	100	-	100	100	100
1-Methylnaphthalene	-	-	-	1000	1000
2-Methylnaphthalene	-	-	-	1000	1000

Other standards have the following concentrations:
Chem Service:

G-1160	Decafluorobiphenyl	1000 µg/mL
F-904AS	Decafluorobiphenyl	2000 µg/mL

O2SI		
000387-03	Decafluorobiphenyl	5000 ug/mL
NSI:		
1288	1-Methylnaphthalene	5000 µg/mL
0562	2-Methylnaphthalene	1000 µg/mL

12.8.2 The alternate check may be made from AccuStandard 610-QC or 610-QC-FL and the appropriate surrogate and solvent.

13.0 INSTRUMENT CALIBRATION AND PERFORMANCE

13.1 Instrument Setup and Configuration.

13.1.1 Recommended system setup.

13.1.2 Initial flow rate may be set to 1.5 mL/min with a 50% Acetonitrile and 50% HPLC water gradient. The gradient after this point is generated upon installation of a new column. A general gradient may be:

Time	HPLC water	ACN
5.00	50	50
12.00	10	90
20.00	0	100
24.00	50	50

13.1.3 The DAD is programmed throughout the run cycle to shift monitoring wave lengths. The basic setup is as follows:

Decafluorobiphenyl (surrogate) is monitored at 224 NM

2-Methylnaphthalene, Fluorene, Phenanthrene, Benzo (b) fluoranthene, Benzo (a) pyrene, and Indeno (1,2,3-cd) pyrene are monitored at 250 NM.

Anthracene, Benzo (k) fluoranthene, Fluoranthene and Pyrene analytes are monitored at 234 NM

Acenaphthylene, Acenaphthene, Dibenzo (a,h) anthracene, and Benzo (g,h,i) perylene analytes are monitored at 270 NM

Naphthalene, 1-Methylnaphthalene, Benzo (a) anthracene, and Chrysene analytes are monitored at 230 NM

13.1.4 The fluorescence detector is programmed to change emission levels and excitation throughout the run. The basic setup is as follows:

Initial settings EX 230 EM 330 for Naphthalene analytes

Changed to EX 210 EM 314 for Acenaphthene, Fluorene

1-Methylnaphthalene and 2-Methylnaphthalene analytes

Changed to EX 250 EM 368 for Phenanthrene and Anthracene analytes

Changed to EX 237 EM 440 for Fluoranthene and Pyrene analytes

Changed to EX 277 EM 376 for Benzo(a)anthracene and Chrysene analytes

Changed to EX 255 EM 420 for Benzo(b)fluoranthene, Benzo(k)fluoranthene and Benz(a)pyrene analytes

Changed to EX 230 EM 453 for Dibenz(a,h)anthracene, Benzo(ghi)anthracene and Indeno(1,2,3-cd)pyrene analytes

NOTE: Acenaphthylene and Decafluorobiphenyl are transparent to the emission at its elution time.

13.2 An external standard technique is used to calibrate the instrument. The calibration is obtained by analyzing the standards using the same method used for samples. Each standard must contain the same analytes, but at different concentration levels. A minimum of five concentration levels is analyzed for each analyte. Presently, an average calibration is used in which the ratio of the peak area of the target analyte in the sample or sample extract is compared to a similar ratio derived for each calibration standard. This ratio is termed Response Factor (RF) and all analytes must have a relative standard deviation (RSD) of 20% or less before the system can be considered calibrated. If the average calibration is not used, the following linear calibration technique may be used as an alternative to calibrate the system. The area counts of each peak along with the concentration of that particular analyte is used to plot a linear calibration curve. The correlation coefficient (r) for each compound of interest must be 0.995 or greater before the system can be considered calibrated. If the system is calibrated, a check standard prepared from a second source is used to verify the calibration. This check must be within 15% of the true concentration for both average and linear calibrations.

13.3 The HPLC^{3D} ChemStation is an instrument control, data acquisition and evaluation system for HP liquid chromatography. ChemStation and Target each offer the standard report calculations: ESTD, and ISTD. Quantification calibration features such as multi-level calibration, multi-signal calibration, multi-internal standards, multi-time reference peaks, and calibration bracketing are available. Presently, an average calibration is used for calibration of the HPLC system.

13.4 Prior to analysis of samples

13.4.1 The HPLC system must be stabilized prior to use. This is checked by observing that pump pressure ripple is within -2% to 2% range. This value displays proper mixing and shows that all solvents have been degassed.

13.4.2 Before samples can be analyzed, the base line must be stable with little or no background noise.

13.4.3 The continuing calibration check standard must pass ±15% of true value.

13.5 A hard copy of the continuing calibration standard and the runlog are maintained with each group of samples.

13.6 The calibration range varies depending on the analyte. Refer to ALPHA LIMS for correct calibration ranges. These are the current levels and are sample dependent. They may change to reflect responses found in samples.

13.7 Currently, confirmation analysis is performed with a Fluorescence detector (FLD) and spectral comparison. Analytes are considered confirmed when the representative response from the primary detector (DAD) and the confirmation detector (FLD) are within the appropriate retention time windows. The confirmation analyte mass normally is within a 30% difference from that of the primary detector. However, due to matrix interference and co-eluting peaks, analytes may be considered suspect and are narrated accordingly. The values reported are from the primary detector. The confirmation detector is used for qualitative purposes only.

13.8 For most DOE clients, some target analytes whose concentrations greatly differ between the primary and confirmation analysis (greater than 40% difference) are flagged with a "P" qualifier. Because both columns or detectors indicated an acceptable peak in the appropriate retention time window for these analytes, the analytes are reported as positive results. Due to the high percent difference between the two columns, it is indicated as such on the appropriate Form I with the "P" qualifier. Those analytes reported with a percent difference greater than 40% but less than 70% are qualified as presumptive evidence of the presence of the material. Analytes reported with a percent difference greater than 70% should be qualified as undetected.

13.9 Samples with responses for analytes on both columns or detectors that indicated an acceptable peak within the retention time window and acceptable concentration match maybe qualified with an "X" qualifier if the result is suspected to be matrix interference. Although method criteria has been satisfied for reporting a positive result for these analytes, the results are considered a false positive due to matrix interference and are indicated as such on the appropriate Form I with the "X" qualifer.

14.0 ANALYSIS AND INSTRUMENT OPERATION

14.1 Check standards and calibration standards are prepared as specified in the current recipe. All standards are directly injected into the HPLC system by the auto sampler. All samples are extracted per GEL SOPs "Extraction of Semivolatile and Nonvolatile Organic Compounds from Soil, Sludge and Other Miscellaneous Samples" (GL-OA-E-010) for solids, and "Extraction of Semivolatile and Nonvolatile Organic Compounds from Groundwater, Wastewater, and Other Aqueous Samples" (GL-OA-E-013) for liquids.

14.2 The run sequence is entered into the ChemStation software with the proper QC bracketing of each group of samples. Multiple injections from a sample vial is allowed. The following is a suggested sequence of QC and samples:

14.2.1 Instrument blank
14.2.2 Check standard
14.2.3 Method blank
14.2.4 LCS
14.2.5 LCS DUP
14.2.6 MS of 14.2.8
14.2.7 MSD of 14.2.8
14.2.8 First sample
14.2.9 Second sample
14.2.10 Third sample through fifth sample
14.2.11 Check standard
14.2.12 Sixth sample through fifteenth sample
14.2.13 Check standard
14.2.14 Repeat steps 14.2.12 through 14.2.13 for every group of 10 samples.
14.2.15 Always end the sequence with a check standard.
14.2.16 For batches of more than 20 samples, repeat steps 14.2.2 through 14.2.14 as needed.

NOTES:

1. Every analytical run of 10 samples is bracketed with a check standard. After every 10 samples, another check standard is analyzed.

2. At least daily, an instrument blank is run to verify the instrument and the solvents used by the instrument.

14.3 Daily or for each group of samples run, a runlog will be generated displaying which samples were run and in what order.

14.4 General Operation of the HPLC System.

14.4.1 Allow system to warm for 15 minutes after turning on all pumps and detectors to allow instruments to be flushed thoroughly and the internal temperatures of the detectors to equalize.

14.4.2 Once the instrument has been allowed to warm up, purge each channel for approximately 5 to 10 minutes of any air bubbles that may be present. Then allow the instrument to equilibrate to operational pressure for a minimum of 15 minutes or 5 times column void time. Monitor pump pressure difference prior to stating analysis.

14.4.3 Verify column is preconditioned prior to starting the run sequence. The method has a built in post column flush to precondition column between samples. A preconditioned column back pressure will be approximately 160 BAR.

14.4.4 If back pressure exceeds 250 BAR, column or system cleaning should be performed to prevent over pressurizing the system and possible column damage, or the column is replaced.

14.4.5 1 BAR equals 14.35 PSI.

14.5 System Operations

14.5.1 Startup

14.5.1.1 Check that the vacuum degasser is ON and operating.

14.5.1.2 Check all solvent containers and refill as necessary. Empty any waste containers that are greater than ¾ full.

14.5.1.3 Start system by selecting "System On" from the instrument sub menu.

14.5.1.4 Monitor pump pressure difference. When difference is in -2% to 2% range (usually stabilizes at about 0.5%), system is ready to start analysis.

14.5.2 For system shutdown select "System Off" from instrument sub menu. This will turn off all pumps and detectors. For long shutdowns also turn off both helium and air tanks.

14.6 Presently the HPLC 1100 system is configured for a 20 µL injection. This can be changed through the instrument sub menu, but should not be changed because present method and MDLs were performed at this setting. If the injection volume is changed, a new calibration must be run.

14.7 When Running Multiple Samples

14.7.1 Place all samples on the sample tray.

14.7.2 Verify run sequence against sample locations in the trays.

14.7.3 In the sequence table enter starting through ending sample if performing a partial run to prevent possible over writing of data. When starting a new sequence this step is not required.

14.7.4 Start system by selecting "Run Sequence" from run control main menu.

14.8 System is designed for minimal maintenance; however, whenever repairs are required consult manufacturer's technical manual for guidance.

14.9 The data report will be client specific. The Target software is capable of generating custom reports based on the client's needs.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

For all routine and nonroutine maintenance see applicable technical manual.

16.0 DATA RECORDING, CALCULATION AND REDUCTION METHODS

16.1 All raw data files are transferred to the server and magnetically backed up. A computer printout is generated for the data review process. Sample data, runlogs and sequence logs are generated by the system before, during or after the instrument has completed the analysis. For each group of samples all data is placed in a folder and that batch number, date run and instrument shall be placed on the front cover and/or on the file tab. Also placed in the folder is a copy of the retention time window study for that day, prep data report, a copy of any applicable nonconformances, and any other appropriate data.

16.2 The Target software is set up to calculate concentrations of sample extracts. When the raw data is entered into LIMS, a final data report is generated which includes all prep factors. (It may or may not include a percent moisture).

16.3 Upon completion of all reviews, all records are filed for approximately six months. After this period, all records are then moved to the long term storage area.

16.4 The following calculations are used to generate sample results when using Method 8310:

16.4.1 Initial Calibration:
A calibration of response factors or calibration factors is applied for an average calibration, which uses a ratio of area to concentration. A calibration plot of peak area versus concentration is used as an alternative and the calibration curve applied is linear.

16.4.2 % RSD:
The percent relative standard deviation (RSD) should be less that 20% for each compound. However, the %RSD for each individual analyte must be less that 15%.

$$\%RSD = \frac{SD}{\bar{X}} \times 100$$

Where:

RSD = relative standard deviation
X = mean of 5 or more initial RFs for a compound
SD = standard deviation of average RFs for a compound

$$SD = \sqrt{\sum_{c=1}^{n} \frac{\left(x_i - \bar{x}\right)^2}{N-1}}$$

16.4.2.1 If the % RSD of any compound is 20% or less, then the relative response factor is assumed to be constant over the calibration range and the average relative response factor may be used for quantitation. If the %RSD for any compound is greater that 20%, a calibration curve of peak area versus concentration is made and the curve applied is a linear fit.

16.4.2.2 If the analyst chooses to use linear regression, he/she must not force the calibration line through the origin.

16.4.3 Instrument Values

RF = A/C

Where:

A = peak area of the analyte detected

C = concentration of the analyte detected.

y = mx

Where:

y = area of target analyte detected

m = slope of line determined by initial calibration

x = concentration

16.4.4 Sample Result: (This calculation is performed by the LIMS rather than the instrument software.)

SR = IV • PF • DF

Where:

IV = Instrument value

PF = Preparation factor:

$$PF_{solid} = \frac{(\text{final extract weight/sample weight})}{(100 - \%\text{moisture}/100}$$

PF_{liquid} = (final extract volume/sample volume)

DF = Dilution factor

SR = Sample result

17.0 QUALITY CONTROL REQUIREMENTS

17.1 Before analysis of any samples, the instrument must be calibrated, and the RSD for the averaged calibration must be less than or equal to 20%, or the calibration curve correlation coefficient (r) must be at or above 0.995 if a linear calibration curve is applied. A Calibration Verification Standard (CVS) is used to verify the calibration. Each day the check standard must be analyzed and be within 15% of the true value. A CVS must be analyzed before and after each batch to verify the calibration curve. If at any time the standard fails, a second run will be performed to verify the first standard. If the second standard also fails, the cause must be investigated and

corrected prior to running any additional samples. All samples not bracketed by valid CVS shall be rerun to confirm the original data.

17.2 A method blank is used to determine background concentrations of analytes of interest that have potential to interfere with the sample analysis. These blanks run with each batch of 20 or less samples. All analytes of interest must be below present PQL to meet the quality control requirements.

17.3 A laboratory control sample and sometimes a laboratory control sample duplicate are run for each batch of 20 samples or less. The accuracy and precision of the extraction procedure may be monitored with these samples. Sample duplicates and sample spikes are also used for this purpose. If matrix spike and matrix spike duplicate recoveries are unacceptable, but the LCS recoveries meet current control limits, the interference shall be reported with a text comment added explaining matrix interference. If the matrix spike, matrix spike duplicate and LCS recoveries are outside of the acceptable ranges, the entire batch must be re-extracted and rerun.

17.4 Decafluorobiphenyl (or other suitable surrogate) is added to all samples that undergo extraction. The surrogate is used to continuously monitor the sample extraction process. If the surrogate falls outside acceptable limits, that sample will be re-extracted. If the surrogate recovery fails a second time, the failure is attributed to matrix interference. A text comment is added to the data, and a non-conformance may be submitted.

17.5 The retention time window is established on a daily basis by using the initial calibration check standard. See GEL SOP "Establishing Retention Time Windows for Gas Chromatographic Analysis" (GL-OA-E-001). To report a concentration from the external calibration table, the retention time of that particular analyte must be within its established window.

17.6 Any positive identification and quantification must be supported by the second detector (FLD) unless the concentration is below detector range. Any target analyte or surrogate that falls within its retention time windows is confirmed.

17.7 Most DOE clients have contract requirements that mandate that the data must have a passing LCS. If this not met, the samples must be re-extracted.

18.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

18.1 After completion of run data is collected and raw values are entered into LIMS, a data review check is then generated. The analyst places the case narrative-data review sheet along with prep sheet and all raw data into a folder marked with the batch number, date run, and instrument used. After the analyst reviews the data and other folder contents, a peer review is done by a data reviewer or qualified analyst. The batch is then sent to "Done" status in ALPHA LIMS.

18.2 Analyst review: The analyst checks all raw data along with the ALPHA LIMS calculations. The analyst also verifies that the check standards pass for the analytes of interest. If a target compound is detected above PQL, that compound is checked against retention time windows. If it is within the acceptable range, this hit is verified with the second detector. If, while reviewing the data, the analyst detects a target concentration above the DAD calibration range, the sample is rerun at a suitable dilution.

18.3 Data Review level review: The data reviewer review ensures that the concentrations appearing as raw data are entered correctly into the LIMS. The

validator verifies that check standards are within 15% of true value and that the LCS and its duplicate and all surrogates are within acceptable ranges. The validator also checks date, time, dilution factors, and analyst initials against the data report. If everything is acceptable, the validator initials each quant report and all other appropriate documentation and routes the data package to the appropriate person to send it to "Done" status in ALPHA LIMS.

19.0 RECORDS MANAGEMENT

19.1 All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

19.2 All standards are recorded in ALPHA LIMS.

20.0 LABORATORY WASTE HANDLING AND DISPOSAL: SAMPLES, EXTRACTS, DIGESTATES AND REAGENTS

For the proper handling and disposal of sample and reagent wastes from this procedure, refer to the "Laboratory Waste Management Plan" (GL-LB-G-001).

21.0 REFERENCES

21.1 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1 (Part 4) Section B, SW846, 3rd edition. Method 8310, "Polynuclear Aromatic Hydrocarbons," Revision 0, September 1986; and Method 8000B, "Determinative Chromatographic Separations," Revision 3, December 1996. US EPA Office of Solid Waste and Emergency Response, Washington, DC.

21.2 Hewlett-Packard Series 1100 Auto Sampler Manual

21.3 Hewlett-Packard Series 1100 Diode Array Detector Manual

21.4 Hewlett-Packard Series 1100 Fluorescence Detector Manual

21.5 Hewlett-Packard Series 1100 HPLC System Manual

21.6 Hewlett-Packard ChemStation Software Manuals

21.7 HPLC for Environmental Analyses, Hewlett-Packard Publication number 12-5091-9750E (5/94)

21.8 Target Data Analysis Software

21.9 Data Validation Standard Operating Procedures for CLP Routine Analytical Services. USEPA Region IV Science and Ecosystem Support Division of Quality Assurance Athens, Georgia, Revision 21, July 1999.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

POLYCHLORINATED BIPHENYLS

(GL-OA-E-040 REVISION 6)

APPLICABLE TO METHODS:
EPA SW-846 Methods 8000B and 8082
EPA 608

PROPRIETARY INFORMATION

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1.0 STANDARD OPERATING PROCEDURE FOR POLYCHLORINATED BIPHENYLS

2.0 METHOD CODES

2.1 EPA SW-846 Methods 8000B and 8082

2.2 EPA 608

3.0 METHOD OBJECTIVE AND PURPOSE

This is a gas chromatographic procedure for quantitatively determining certain polychlorinated biphenyls. The analytical guidance for the detection and quantitation of the applicable polychlorinated biphenyls has been taken from Methods 8082 and 8000B "Test Methods for Evaluating Solid Waste," EPA Manual SW-846, June 1997, Final Update III.

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 The following analytes can be quantitatively determined by this procedure:

Aroclor 1016	Aroclor 1221	Aroclor 1232
Aroclor 1242	Aroclor 1248	Aroclor 1254
Aroclor 1260	Aroclor 1262	Aroclor 1268

PCB Congeners (see Appendix 1)

4.2 This method applies to the following matrices:

4.3.1 Groundwater
4.3.2 Wastewater
4.3.3 Soil
4.3.4 Sludge
4.3.5 Miscellaneous matrices
4.3.6 Oil
4.3.7 Filters/Swipes

4.3 This method summarizes the procedures necessary to analyze a sample extract for Polychlorinated Biphenyls by gas chromatography. Laboratory control samples (LCS) and matrix spike/matrix spike duplicates (MS/MSD) are used to verify the accuracy and precision of the extraction technique.

5.0 METHOD SCOPE AND PERFORMANCE CHARACTERISTICS

5.1 The calibration ranges for Aroclors and Congeners are compound specific. The lowest concentration calibration standard is used as the quantitation limit.

5.2 The test concentration ranges are:

5.2.1 The tested concentration ranges for liquid matrices are listed below. Please note that these may change and are listed here for guidance only. These limits include an ideal prep factor and are based on a typical calibration.

Compound	Concentration Range
4-CMX	0.01 ug/L – 0.4 ug/L
DCB	0.01 ug/L – 0.4 ug/L
Aroclor 1016	0.1 ug/L – 4 ug/L
Aroclor 1221	0.1 ug/L – 4 ug/L
Aroclor 1422	0.1 ug/L – 4 ug/L
Aroclor 1248	0.1 ug/L – 4 ug/L
Aroclor 1254	0.1 ug/L – 4 ug/L
Aroclor 1260	0.1 ug/L – 4 ug/L
Aroclor 1262	0.1 ug/L – 4 ug/L

Aroclor 1268	0.1 ug/L – 4 ug/L
Congeners	0.01 ug/L – 0.5 ug/L

5.2.2 The tested concentration ranges for solid matrices are as follows.

Compound	Concentration Range
4-CMX	0.33 ug/Kg – 13.3 ug/Kg
DCB	0.33 ug/Kg – 13.3 ug/Kg
Aroclor 1016	3.3 ug/Kg – 133 ug/Kg
Aroclor 1221	3.3 ug/Kg – 133 ug/Kg
Aroclor 1422	3.3 ug/Kg – 133 ug/Kg
Aroclor 1248	3.3 ug/Kg – 133 ug/Kg
Aroclor 1254	3.3 ug/Kg – 133 ug/Kg
Aroclor 1260	3.3 ug/Kg – 133 ug/Kg
Aroclor 1262	3.3 ug/Kg – 133 ug/Kg
Aroclor 1268	3.3 ug/Kg – 133 ug/Kg
Congeners	0.33 ug/Kg – 16.7 ug/Kg

5.3 Method Detection Limit (MDL) studies for Polychlorinated Biphenyls are performed annually.

5.4 Precision is determined by the Relative Percent Difference (RPD) between the Laboratory Control Sample (LCS) and the Laboratory Control Sample Duplicate (LCSD), when required, or the Matrix Spike (MS) and the Matrix Spike Duplicate (MSD). The RPD is determined through Statistical Process Controls (SPC), which are updated on an annual basis.

5.5 Accuracy is determined by the percent recovery on LCSs and MSs and the control ranges are determined through SPC limits that are updated annually.

6.0 REFERENCES

6.1 EPA 608 and Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/Chemical Methods, Volume 1 (Part 2 and Part 3) Section B. SW-846, Third Edition. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460, June 1997.

6.1.1 Method 8000B, "Determinative Chromatographic Separations," Rev. 2, Dec. 1996.

6.1.2 Method 8082, "Polychlorinated Biphenyls (PCBs) by Gas Chromatography," Revision 0, December 1996.

7.0 INTERFERENCES TO THE METHOD

7.1 Interference by phthalates can pose a major problem in PCB determinations and quantitation. These compounds generally appear in the chromatogram as large late-eluting peaks. Common flexible plastics contain varying amounts of phthalates that 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.

7.2 Interference for phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

7.3 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting peaks. Sulfur contamination should be expected with sediment samples. Method 3600 is used for sulfur removal.

7.4 The presence of oil or petroleum wastes in the sample will create interferences with target analytes in the chromatogram. The majority of these contaminants can be removed by using the alumina column cleanup procedure in method 3611B. This involves passing the sample extract through a glass pipet with a glass wool plug that contains approximately 10 – 12 g of neutral pH alumina. The sample extract is recovered by gently forcing air through the column with a pipet bulb. There is some loss of sample volume with this procedure since the column is not rinsed with any additional solvent, which would result in a dilution of the extract. Any associated quality control samples, such as method blanks and laboratory control samples, must also undergo this procedure. This is to ensure that any additional contamination has not been introduced and that the target analytes have not been affected by the cleanup procedure.

8.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

8.1 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and client sample MSDS forms are maintained in the laboratory.

8.2 Personal protective equipment

8.2.1 Gloves are required when handling the chemicals in this procedure. Latex gloves are approved for this procedure.

8.2.2 Laboratory coats and safety glasses should also be worn.

8.3 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling.

8.4 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.5 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

8.6 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the GEL Safety Officer.

8.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located throughout the lab. Training is available on the proper operation of this equipment.

9.0 CAUTION WARNINGS

The helium, nitrogen and hydrogen tanks should be replaced when pressure drops to approximately 500 psi. It is recommended that the injection port septum be changed daily.

10.0 APPARATUS AND MATERIALS; REAGENTS; EQUIPMENT AND INSTRUMENTS

10.1 Ancillary equipment may include:

10.1.1 Volumetric flasks

10.1.2 Pasteur pipettes

10.1.3 Microliter syringes (10, 25, 50, 100, 250, 500, 1000)

10.1.4 Capillary cleaving tool

10.1.5 2 mL amber and clear auto sampler screw-capped vials with Teflon-lined septa or 2 mL amber and clear auto sampler crimp top vials with 500 uL inserts.

10.1.6 Supeltex 0.5 and 0.8 mm ferrules (or equivalent)

10.1.7 Glass Y-splitter or stainless steel column connector

10.2 Reagent, chemicals and standards

10.2.1 Solvents: Acetone, Hexane, Isooctane, and Toluene (pesticide grade or equivalent)

10.2.2 For chemical standards, see Section 14.0

10.3 Instrumentation

10.3.1 GC: HP6890 Series Plus with electronic pressure control
HP7683 GC Auto Sampler

10.3.2 Columns:

J&W Scientific DB-17MS	0.25 micron x 30 meters
J&W Scientific DB-5	0.25 micron x 30 meters
Restek CLP1	0.25 micron x 30 meters
Restek CLP2	0.20 micron x 30 meters

NOTE: The instrumentation and columns listed above are merely the recommended instrumentation and columns for use with the method.

11.0 SAMPLE HANDLING AND PRESERVANTION REQUIREMENTS

11.1 Samples must be collected in an amber glass bottle with a Teflon-lined cap. The collection containers are bought precleaned from a certified vendor.

11.2 All liquid samples have a holding date of seven days from the time of collection to be extracted while all solid samples have fourteen days from the collection date to be extracted Samples are protected from light and stored at 4° ± 2°C after collection. Once extracted, the extract must be analyzed within forty days. However, during this period of time, the extracts are refrigerated at 4° ± 2°C in amber vials with Teflon sealed screw caps. When holding dates are missed, the data is automatically flagged by the computer when inputting data.

12.0 SAMPLE PREPARATION TECHNIQUES

12.1 See "Extraction of Semivolatile and Nonvolatile Organic Compounds from Ground Water, Waste Water, and Other Aqueous Samples" (GL-OA-E-013), and "Extraction of Semivolatile and Nonvolatile Organic Compounds from Soil, Sludge and Other Miscellaneous Samples"(GL-OA-E-010).

NOTE: It is assumed that material within the sample container is considered "the sample." Removal of any extraneous material (twigs, leaves, large rocks, etc.) must be documented in the case narrative and sample extraction logbook.

12.2 See "Extraction of Semivolatile and Nonvolatile Organic Compounds from Groundwater, Wastewater, and Other Aqueous Samples" (GL-OA-E-013), and "Extraction of Semivolatile and Nonvolatile Organic Compounds from Soil, Sludge and Other Miscellaneous Samples" (GL-OA-E-010).

13.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

13.1 In order to maintain the gas chromatograph's columns and detectors, the gases should be changed when the tank pressure is below 500 psi. The gas chromatograph's septum in the injection port should be changed daily. Column maintenance is performed when baseline rise is present or when the column becomes contaminated.

13.2 Routine Maintenance

COMPONENT	*DAILY*	*WKLY*	*MTHLY*	*AS NEEDED*	*ANNUALLY*
Injector septum	X				
Gases				X	
Column Maintenance				X	
Detector Wipe Test					X
Detector Cleaning				X	

13.3 Non-routine Maintenance

13.3.1 When a check standard fails, the standard is examined for signs of evaporation or degradation. If nothing is found, column maintenance should be performed. Approximately one loop of each column, or two loops of guard column should be cleaved. The instrument is then baked out until an acceptable baseline is obtained. If an acceptable baseline is not obtained, the column is leaking and column maintenance must be performed again.

13.3.2 When contamination occurs, first replace or clean the auto sampler syringe. If contamination is still present, column maintenance should be performed. If contamination is still present after column maintenance has been performed and the system has been cleaned thoroughly, replace the column. The column must then be leak checked and baked. The instrument must then be checked to determine if the problem is solved and if the instrument is stable. If not, the in-house service technician is called.

13.4 When maintenance is done on the instrument, it must be recorded in the maintenance logbook. It must be initialed and dated.

14.0 PREPARATION OF STANDARD SOLUTION AND QUALITY CONTROL SAMPLES

14.1 Source Standard Solutions

14.1.1 Source standard solutions are purchased from Restek, ChemService, Protocol, AccuStandard, and other certified vendors. These standards are traceable to National Institution of Standards and Technology (NIST) standards. The source standards are received from the company Purchasing Agent. The standard is given a unique identifying number for that day and is recorded in the Standard notebook or ALPHALIMS. This standard expires either six months from the date opened, one year from the date received if not opened, or on the vendor expiration date, whichever comes first.

14.2 For guidance on standard documentation, refer to "Laboratory Standard Documentation" (GL-LB-E-007).

14.3 For standards traceability, refer to "Organic Standards Preparation and Traceability" (GL-OA-E-002).

14.4 All stock standard solutions expire six months from date prepared/opened if no expiration date is provided by the vendor. All other standard solutions must be replaced after six months.

15.0 INSTRUMENT CALIBRATION

15.1 The instrument should be checked for cleanliness and stability prior to analyzing calibration standards. The standards are loaded onto the auto sampler with the lowest standard being analyzed first to prevent carryover.

15.2 An external standard technique is used to calibrate the instrument. Calibration is obtained by analyzing the standards using the same method used for samples. Each standard must contain the same analytes, but at different concentration levels. The area counts of each peak along with the concentration of that particular analyte can then be used to plot a calibration curve. For multi-component peaks such as PCBs, major peaks are chosen to represent the pattern. PCBs require a minimum of five peaks except Aroclor-1221 that requires a minimum of three peaks for quantitation. The area counts of these peaks are then used to obtain a curve. Note that the same peaks are to be used for each concentration level and that a curve is obtained for each peak. The same peaks used in the calibration of the multi-component compounds must be used in any quantitation associated with that calibration curve. The chosen peaks must be at least 25% of the height of the largest Aroclor peak.

15.3 The initial calibration consists of two parts.

15.3.1 A standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other Aroclor mixtures. This standard is used to demonstrate linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. It can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in the sample. Therefore, an initial five-point calibration is performed using this mixture.

15.3.2 Standards of the other Aroclors are necessary for pattern recognition. These standards are also used to determine a single point calibration factor for each Aroclor, assuming that the Aroclor 1016/1260 has been used for detector response. The standards for these Aroclors should be analyzed before the analysis of any samples and may be analyzed before or after the analysis of the five 1016/1260 standards.

15.3.3 In certain situations the analyst has the option to employ a five-point calibration for all Aroclors and Aroclor 1016/1260 calibration.

15.4 Updating of the calibration curves is done automatically by the Target system. Because the samples are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated. Also calculate the mean calibration factor and the relative standard deviation for each analyte at each standard concentration using the formula below.

NOTE: Certain specific clients (i.e., Navy) require that both columns meet all acceptance criteria for each analyte of interest before running samples.

15.4.1 Calculate the calibration factor for each analyte at each concentration as:

$$CF = \frac{\text{Peak Area of the Compound in the Standard}}{\text{Mass of the Compound Injected (in nanograms)}}$$

15.4.2 Calculate the mean calibration factor for each analyte as:

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where n is the number of standards analyzed.

15.4.3 Calculate the standard deviation and the RSD of the calibration factor for each analyte as:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - \overline{CF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{CF}} X 100$$

If the percent relative standard deviation (%RSD) of the calibration factor is ≤ 20% over the working range, linearity through the origin can be assumed, and the mean calibration factor can be used to quantitate sample results. When this is not the case, linearity cannot be assumed and the analyst must use a calibration curve. In the case of EPA 608, %RSD must be ≤ 10%.

15.5 If the analyst chooses to use linear regression, he/she must not force the calibration line through the origin.

15.5.1 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response
a = slope of line (also called the "coefficient of x")
x = concentration of the calibration standard
b = the intercept

15.5.2 The analyst should not force the line through the origin, but have the intercept calculated from the five data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0, 0) as a sixth calibration point.

15.5.3 The regression calculation will generate a correlation coefficient (R) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, R must be > 0.99. The calculated intercept value needs to be evaluated before reporting sample results. If the system you are using calculates the coefficient of determination (R^2), the value must be ≥ 0.9801.

15.5.4 A positive value for the intercept indicates that there is some threshold instrument response that is the limiting factor in establishing linearity. A negative intercept value can be transformed into an x-intercept value that represents a threshold concentration, which is the limitation. If the intercept is positive, then, as a general rule, results where the instrument response is less than three time (3x) the intercept value may be unreliable. This will afford some protection against false positive results. If the intercept is negative, results below the concentration of the lowest concentration calibration standard may be unreliable.

NOTE: For Navy clients, these adjustments to the quantitation limits will apply to all samples analyzed using the regression line.

15.5.5 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y - b)}{a}$$

15.6 A minimum number of five calibration standards is required by the method.

15.7 Continuing Calibration

15.7.1 The initial calibration curve must be checked and verified prior to conducting any sample analysis. This is accomplished by analyzing a calibration standard of Aroclor 1016/1260 that is at a concentration near the midpoint concentration for the working range of the GC. The standard must also be injected at intervals no less than once every twenty samples (after 10 is recommended to minimize the number of samples requiring re-injection when the QC limits are exceeded) and at the end of the analysis sequence. The continuing calibration check standard must be a second source standard. It must be obtained from a second supplier. This will determine the validity of the initial calibration on a daily basis.

15.7.2 Calibration verification for linear calibrations involves calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equation below to calculate % Drift or % Difference.

$$\% \text{ Drift} = \frac{\text{Calculated Concentration - Theoretical Concetration}}{\text{Theoretical concentration}} \times 100$$

Where the calculated concentration is determined using the calibration factor or response factor from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{\overline{CF} - CF_v}{\overline{CF}} \times 100$$

Where:

CF_V = response factor from current verification check standard.

If this criteria is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration will be generated.

15.7.3 Each sample must be bracketed with an acceptable continuing calibration standard. The continuing calibration check standard must pass ±15% of the true value. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last acceptable standard must be re-injected.

15.7.4 When simultaneous analyses are performed from a single injection, it is not practical to designate one column as the primary and the other as confirmatory. Since the calibration standards are analyzed on both columns, the results for both columns must meet the calibration acceptance criteria. (See section 21.7)

16.0 INSTRUMENT PERFORMANCE REQUIREMENTS

16.1 Recommended Gas Chromatography Conditions

Detector Temperature: 350° C	Make-up Gas: Nitrogen
Injector Temperature: 250° C	Initial Temperature: 130° C
Column A: CLP Pesticides I	Hold = 0 min
Column B: CLP Pesticides II	Ramp = 25° C/min
Column Flow = 5 mL/min	Final Temperature: 320° C
Det. Flow = 30 mL/min	Hold = 0.5 min
Carrier Gas: Helium	Run Time: ≈ 8 min

NOTE: Slight variations may be needed as column length changes. In addition, please note that other columns and analytical parameters may be used.

16.2 Before samples can be analyzed the baseline must be stable with little or no background noise. The continuing calibration check standard must pass ±15% of the true value.

16.3 A hard copy of the continuing calibration check standard is kept with the quality control samples and client samples that were analyzed after it. After every ten samples a continuing calibration check standard must be analyzed and be ±15% of the true value. If not, the system must be inspected for malfunctions. All samples must be bracketed by passing check standards.

The results from the bracketing standards must meet the calibration criteria as specified above. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard that last met the QC criteria must be evaluated to prevent mis-quantitations and possible false negative results and re-injection of the sample extracts may be required. More frequent analysis of standards will minimize the number of sample extracts that would have to be reinjected if the QC limits are violated for the standard analysis.

However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit, i.e., >15%, and the analyte was not detected in the specific samples analyzed during the analytical shift, then the extracts for those samples do not need to be reanalyzed, as the verification standard has demonstrated that the analyte would have been detected were it present. In contrast, if the analyte above the QC criteria was detected in a sample extract, then re-injection is necessary to ensure an accurate quantitation. If an analyte was not detected in a sample and the response is more than 15% below the initial calibration response, then re-injection is necessary to ensure that the detector's response has not deteriorated to the point that the analyte would not have been detected even though it was present (i.e., a false negative result).

EXCEPTION: IT IS A NAVY REQUIREMENT THAT ALL NAVY SAMPLES BE RE-ANALYZED IF THIS CHECK FAILS.

16.4 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 QC criteria are exceeded.

17.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

17.1 To establish that the analyst can perform the procedures in an acceptable manner and that the method generates data of acceptable bias and precision, the following operations are performed.

17.1.1 A quality control (QC) check standard must be prepared containing each analyte of interest. It must be prepared from pure standard material or purchased as a certified solution. It must be made from a source independent of that used for calibration.

17.1.2 Four samples must be prepared and analyzed by the same procedures used to prepare and analyze actual samples.

17.1.3 Calculate the average recovery (X) in µg/L and standard deviation of the recovery (S) in µg/L, for each analyte of interest using the four results.

17.1.4 For each analyte compare S and X with the corresponding acceptance criteria for precision and accuracy, respectively, given in the quality control table at the end of the method. If the S and X for all analytes of interest meet the acceptance criteria, the system's performance is acceptable and analysis of actual samples can begin. If any individual S and X exceeds the precision limits or falls out of the range for accuracy, the system's performance is unacceptable for that analyte and a check standard for that analyte must be prepared and reanalyzed. A copy of this data is kept in a file within the Organics Laboratory area.

17.2 Method detection limits are also determined and documented annually. Precision and accuracy are matrix dependent and are documented by means of a Laboratory Control Sample (LCS) and a Laboratory Control Sample Duplicate (LCS DUP). (See Section 5.4 and "Determination of Method Detection Limits" (GL-LB-E-001).

17.3 Analysts are given continual performance evaluation samples as an ongoing assessment of their ability to perform this procedure.

18.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

18.1 Standards, samples, blanks and quality control samples are introduced into the instrument via direct injection. Retention time windows must be centered daily for each analyte. See "Establishing Retention Time Windows for Gas Chromatographic Analysis" (GL-OA-E-001) as to when and how often retention time windows should be established.

18.2 Samples are analyzed in a set referred to as analysis sequence or run sequence. The sequence begins with the initial check standards with the representative multi-component standards for pattern recognition followed by the sample extracts. A mid-level calibration check standard must be analyzed after every 10 extracts and at the end of each run sequence. The sequence ends when all extracts have been injected and analyzed.

18.2.1 The following information is entered for the sample identification:

/Sample ID/Dilution/

18.3 The data is entered into the computer and a data report is generated. The sequence file is created by the analyst on the computer. It lists every injection made by the instrument, in order, for a given date. The raw data along with a

copy of the run sequence, batch sheet, case narrative, and a copy of the retention time window are maintained together.

18.4 Gas chromatographs are used to analyze extracts for PCBs. When the gas chromatograph indicates that it is ready, all temperatures are at their desired starting point. The running indicator light will also come on. When the run is complete, a computer print out of the chromatogram and an external standards table will be printed.

18.5 1.0 µl of the extract is injected into the instrument.

18.6 All HP6890 Gas Chromatographs are equipped with the HP7683 GC autosampler. The digital integrator converts the analog from the instrument to digital information that is processed into a graphic format showing concentration based on peak area.

18.7 The automated sequence is initiated by starting the "run sequence" made in Chemstation, which, in turn, controls the auto sampler.

18.8 Samples containing target analyte concentrations that exceed the linear range of the analyte calibration curve must be diluted. The dilution level should be performed to place the highest analyte concentration between the middle and high points of the calibration curve (on column). If a sample is initially diluted and target analytes are not detected and non-target analytes are not interfering with the analysis, the sample must be reanalyzed at a lower dilution. Analysts should be aware that diluting samples will increase the detection limits for undetected analytes. Random dilutions without due cause are not acceptable. Samples should undergo appropriate clean up methods prior to diluting for observed matrix problems.

19.0 CALCULATIONS AND DATA REDUCTION METHODS

19.1 The concentration of each analyte in an extract can be determined by comparing the response obtained from analyzing the extract to the calibration curve. The concentration of a specific analyte is matrix specific and is calculated as follows:

Aqueous Sample

$$Concentration(\mu g/L) = \frac{(C)(D)(V_t)}{V_i}$$

Where:

C = Concentration (µg/L) calculated by data system from total area substituted into the linear equation derived from the multilevel calibration

D = Dilution factor, if made prior to analysis. If not, D = 1.

V_t = Total volume of the extract in L

V_i = Initial volume of sample in mL

Nonaqueous Samples

$$Concentration(\mu g/kg) = \frac{(C)(D)(V_t)}{W}$$

Where:

C = Concentration (µg/L) calculated by data system from total area substituted into the linear equation derived from the multilevel calibration

D = Dilution factor, if made prior to analysis. If not, D = 1.

V_t = Total volume of the extract

W = Weight of the sample extracted

19.2 A copy of the External Data Table is shown in Appendix 2.

19.3 Results are reported to the nearest one tenth for all matrices.

19.4 The reporting units are micrograms of analyte per liter of sample for aqueous samples, micrograms of analyte per kilogram of sample for soils, and milligrams per liter for TCLPs.

20.0 DATA RECORDING

Data is recorded and calculated by the Target system. It is stored on a remote server. The data is also entered into the Laboratory Information Management System.

21.0 QUALITY CONTROL REQUIREMENTS

21.1 Before analysis of any quality control samples, the instrument must be calibrated. An outside source initial calibration check standard is analyzed to verify that the curve is linear. This outside source check standard must be analyzed every time a new curve is obtained. This check standard must be within ±15% of the true value. A continuing calibration check standard must be analyzed after every ten to verify that the instrument remained calibrated throughout the run. This too must be within ±15% of its true value.

21.2 A method blank is used to determine background concentrations of analytes of interest that have the potential to interfere with sample analysis. These blanks are analyzed with every analytical batch that has a maximum number of twenty samples. The criteria for acceptance is that there are no target analytes of interest present above the practical quantitation limit.

If the analyte of interest is present at a concentration between the MDL and PQL, all data is qualified with a "B" flag and reported. If the analyte of interest is present at a concentration above the PQL and the samples contain the analyte of interest at a concentration of greater than 10 times the concentration found in the blank, the data is qualified with a "B" flag and reported. If the concentration found in the sample is less than 10 times that found in the blank and greater than the PQL, the samples must be re-extracted. If the samples do not contain the analytes of interest, the data is reported.

21.3 A laboratory control sample and its duplicate (when requested) are analyzed with every batch. The accuracy and precision of the extraction and analysis are monitored with these samples. Sample spikes and sample duplicates are also used for this purpose. The criteria for acceptance is that the recoveries must be within the fixed range for any given analyte for a specific matrix. See Section 5.4.

21.4 4-CMX and Decachlorbiphenyl surrogates are added to all extracts including standards. Its acceptance is based on statistically derived limits and is matrix specific. See Section 5.5. 4-CMX is added to all congener analyses.

21.5 The retention time (RT) window must be established using the continuing calibration check standard over a 72-hour period. See "Establishing Retention Time Windows for Gas Chromatographic Analysis" (GL-OA-E-001) for instructions. In order to report a concentration from the external standard table, the retention time of that particular analyte must be within its established window. If not, the concentration is not reported.

21.6 Nonconformance

21.6.1 When running a calibration curve for more than one analyte at a time, some of the analytes may not meet the acceptance criteria. Additional standards containing the compounds that were not acceptable may be analyzed. If the curve still does not meet the acceptance criteria, maintenance should be performed or a new standard may be needed.

21.6.2 If the percent recovery in the matrix or matrix spike duplicate falls outside the established SPC limits for recovery, the analyst should evaluate the LCS recoveries and method blank analyses. If the LCS and method blank analyses do not indicate a problem with the preparation procedures, the matrix spike recoveries may be attributed to matrix effect. Surrogate recovery data should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside the acceptance limits suggest more pervasive analytical problems than problems with the recoveries of either matrix spikes or surrogates alone. Analysts are not required to reanalyze the matrix spikes for failing recoveries, however they should seek additional technical support before deciding not to reanalyze matrix spikes samples.

21.6.3 If the continuing check standard fails any criteria in section 21.1, the analyst must take action to correct the situation. This may be performing any of the maintenance steps described in Section 13 to get the instrument to meet its daily calibration. If all attempts fail the analyst must analyze a new series of calibration standards, thus obtaining a new calibration curve.

21.6.4 If a surrogate in a sample falls outside the acceptance limits, the sample must be re-extracted, unless the failure duplicates in an MS, MSD or sample duplicate. If the surrogate fails the second time, the failure is attributed to matrix interference and the data from the first extraction is reported. When a sample or batch is sent back to be re-extracted, and passes, a nonconformance form must be completed. The form describes the reasons for re-extraction. (See "Documentation of Nonconformance Reporting and Dispositioning, and Control of Nonconforming Items" (GL-QS-E-004).)

21.7 Any positive identification and quantitation of an analyte of interest must be confirmed on a separate column and/or GC/MS. The confirmation column or GC/MS must meet all quality control acceptances described in the method (calibration, retention times, etc.). Calculate the relative percent difference between the two results using the formula:

$$RPD = \frac{|R_1 - R_2|}{R_1 \text{ or } R_2, \text{ whichever is lower}} \times 100$$

21.7.1 Since the same method criteria specified in Sections 21.1 - 21.5, and instrument calibration specified in Sections 15.1 - 15.6 are applied uniformly to both columns, either column can be selected to serve as the primary or confirmatory column.

21.7.2 If one result is significantly higher (>40%), check the chromatograms to see if an obviously overlapping peak is causing an erroneously high result.

21.7.3 If no anomalies are noted, review the chromatographic conditions. If there is no evidence of chromatographic problems, report the result from the primary column. The higher value is reported in all cases, unless a client specifically requests otherwise. As of the effective date of this SOP, no clients receive the lower value.

NOTE: Navy requirements specify that both columns must meet the quality control acceptance criteria and that the confirmed analyte will be reported off the column with the lowest concentration. The higher MDL is also reported.

22.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

22.1 Upon completion of a batch, the analyst enters the data. A data report is generated and it is placed in a folder along with the batch and all other raw data (chromatograms). This folder is given to the peer review analyst for reviewing.

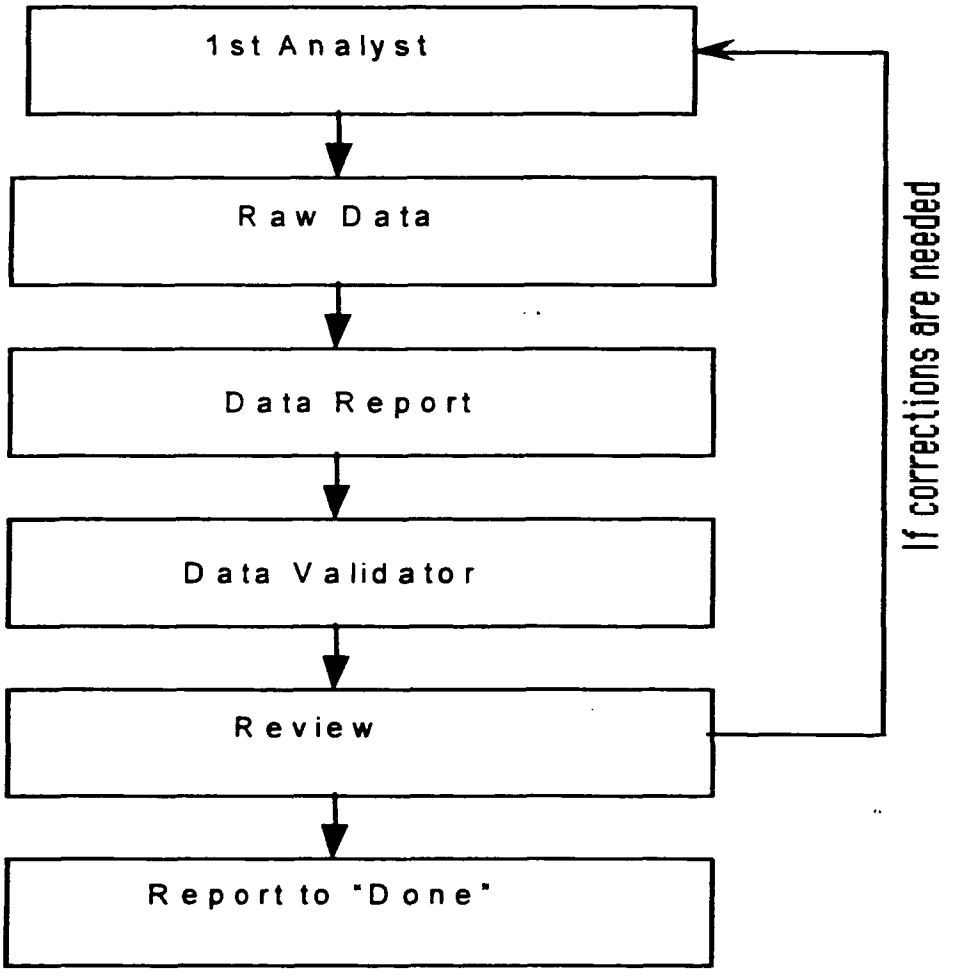
22.2 Levels of review and their responsibilities

22.2.1 First level review - The analyst must check all chromatograms. They will also calculate the percent recoveries for the spike, duplicate, and all surrogate recoveries. They must check to see if the check standard passes for the analytes of interest. If a target compound confirms on the conformation column, it must be checked to see if the retention time of the analyte is within the daily retention time window. The peak's shape must also be checked to ensure that it is indeed a peak and not noise. If the hit meets both of these requirements, its concentration should be reported.

22.2.2 Second level review - The data reviewer or other qualified reviewer must ensure that the concentration that appears in the external standards table is indeed what has been entered into the computer. They must check to see if the calibration check standard is acceptable and if the LCS and its duplicate and the surrogates are all within acceptable ranges. The reviewer must also check the date analyzed, dilution factor, and time of analysis from the raw data against the data report. If everything is acceptable, the reviewer must then initial and date the batch report and the quantitation report, and then complete the checklist to make sure that every item that appears on the review checklist is acceptable. The run log must also be dated and initialed. The data report is then sent to a status of "Done".

22.2.3 To complete a review process, all chromatograms of the calibration check standard, blank, LCS and its duplicate, samples and the spike and/or duplicates of the sample must be present. The batch sheet, sample tracker log, and the data report should all be present.

22.3 A flow chart of the review process follows on the next page:



23.0 DATA TRANSMITTAL

After the review process is complete, Data Management receives the data.

24.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

25.0 LABORATORY WASTE HANDLING AND DISPOSAL: SAMPLES, EXTRACTS, DIGESTATES AND REAGENTS

Refer to the Laboratory Waste Management Plan, GL-LB-G-001 for the proper handling and disposal of sample waste.

APPENDIX 1: LIST OF CONGENERS APPLICABLE TO GL-OA-E-040

2,2',5-Trichlorobiphenyl (18)
2,4'-Dichlorobiphenyl (8)
2,4,4'-Trichlorobiphenly (28)
Heptachlorobiphenyl (170)
Heptachlorobiphenyl (180)
Heptachlorobiphenyl (183)
Heptachlorobiphenyl (184)
Heptachlorobiphenyl (187)
Heptachlorobiphenyl (189)
Hexachlorobiphenyl (128)
Hexachlorobiphenyl (138)
Hexachlorobiphenyl (153)
Hexachlorobiphenyl (156)
Hexachlorobiphenyl (157)
Hexachlorobiphenyl (167)
Hexachlorobiphenyl (169)
Nonachlorobiphenyl (206)
Octachlorobiphenyl (195)
Pentachlorobiphenyl (101)
Pentachlorobiphenyl (105)
Pentachlorobiphenyl (114)
Pentachlorobiphenyl (118)
Pentachlorobiphenyl (123)
Pentachlorobiphenyl (126)
Pentachlorobiphenyl (87)
Tetrachlorobiphenyl (44)
Tetrachlorobiphenyl (49)
Tetrachlorobiphenyl (52)
Tetrachlorobiphenyl (66)
Tetrachlorobiphenyl (77)
Tetrachlorobiphenyl (81)
Dechachlorobiphenyl (209)

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

NITROAROMATICS AND NITRAMINES

BY

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

(GL-OA-E-033 REVISION 8)

APPLICABLE TO METHODS:
EPA SW-846 Methods 8330 and 8000B

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1.0 STANDARD OPERATING PROCEDURE FOR NITROAROMATICS AND NITRAMINES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

2.0 METHOD CODES:

2.1 EPA SW-846 Method 8000B

2.2 EPA SW-846 Method 8330

3.0 METHOD SUMMARY, OBJECTIVE AND PURPOSE

3.1 This is a liquid chromatographic procedure for quantitatively determining trace analysis of explosives residues. The analytical guidance for the detection and quantitation of the applicable Nitroaromatics and Nitramines has been taken from Methods 8330 and 8000B of "Test Methods for Evaluating Solid Waste," EPA Manual SW-846.

3.2 This method applies to ground water, soil, leachates, and miscellaneous matrices. Referenced procedures are 8330 and 8000B of "Test Methods for Evaluating Solid Waste," EPA Manual SW-846.

3.3 The following compounds can be quantitatively determined by this procedure:

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

3.3.1 Pentaerythritol Tetranitrate (PETN) (CAS number 78-11-5), Nitroglycerin (CAS number 55-63-0), and Picric Acid (CAS number 88-89-1) can also quantitatively be determined by this procedure. Nitroglycerin, however, coelutes with 8330 compounds on the primary column. Therefore, a separate set of LCS/LCSD and MS/MSD are extracted and analyzed, and a separate standard is analyzed.

3.4 This method provides the High Performance Liquid Chromatographic (HPLC) conditions for the detection of trace levels of explosive residue. Prior to use of this method, samples must undergo an extraction procedure. (See Appendix 1 for liquids and Appendix 2 for solids). A portion of the extract is injected into the HPLC system. The sample then passes through the reverse phase column that performs analyte separation. The separated analytes then pass through the Diode Array Detector (DAD). The output of the detector is sent to the ChemStation software package that collects, processes and quantifies the signals from the detector into usable data. Analyte confirmation is performed using a cyano (CN^-) column. Due to the coelutions on the cyano column, confirmation analysis is for qualitative purposes only.

4.0 METHOD PERFORMANCE ANALYST VERIFICATION

4.1 For present liquid and solid matrix MDLs and PQLs, see Group Leader for current MDL tables.

4.2 Method Precision: Refer to current SPC charts for RPD limits.

4.3 LCS %Recovery and LCS-LCSD RPD: Refer to current SPC charts for % recovery limits and RPD.

4.4 Method Bias: See SPC limits for current surrogate recovery.

5.0 DEFINITIONS

5.1 HPLC - High performance liquid chromatography

5.2 DAD - Diode array detector

5.3 UV 3^d - Three-dimensional view of UV Spectrum (used for compound verification.)

5.4 ChemStation - Software package used to control HPLC instruments including data acquisition and temporary storage.

5.5 Calibration Blank - A volume of reagent water without the analytes, internal standards, or surrogates used within the calibration curve.

5.6 Calibration Standard (CAL) - A solution prepared from the primary stock solution. The CAL solutions are used to calibrate the instrument.

5.7 Check Standard (CVS/ICV/CCV) - A solution of the method analytes used to evaluate the performance of the instrument with respect to a defined set of criteria. The check standard concentration is at the calibration midpoint and is prepared from a separate source than the calibration standards.

5.8 Matrix Spike (MS) - An aliquot of a known sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed like a sample and its purpose is to evaluate the accuracy of the method.

5.9 Field Duplicate (FD) - Two separate samples collected at the same time, placed under identical conditions, and treated exactly the same way throughout the field and laboratory process.

5.10 Linear Calibration Range (LCR) - The calibrated concentration range over which the instrument response is linear.

5.11 Laboratory Control Sample (LCS) - An aliquot of reagent water to which a known quantity of the method analyte is added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine if methodology is in control.

5.12 Method Blank - An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents and reagents which are used with other samples. The method blank is used to determine if method analytes or other interferences are present in the laboratory environment.

5.13 Sample Duplicate (Dup) - A duplicate of a selected sample. The Dup will demonstrate analytical precision.

5.14 TARGET – Data Analysis Software used to process and store analytical data.

6.0 METHOD VARIATION

6.1 Referenced procedure requires that each organization develop a method of verifying possible explosive compounds. By using the full spectrum of the DAD, positive verification can be supported by comparing the suspect compound spectrum against a compound standard spectrum. Positive verification can be accomplished by a second column confirmation analysis.

6.2 SW-846 method 8330 sample extraction method is incomplete, and detection limits are unattainable. GEL has developed an extraction technique that does obtain the required MDL for solids and is within the acceptable range for liquids. (See Appendices 1 and 2 for extraction procedures.) GEL presently concentrates the extract prior to the addition of water. All MDL studies were performed with this step included, and no recovery problems were encountered.

6.3 For soil extraction procedure - Due to the nature of the calculation in determining final concentration within the laboratory information management system, a correction factor is added to the prep data prior to entering the data. When soil samples are prepped, half of the extraction fluid is discarded in the filtering phase and transferring stage to the concentrator tubes. Due to the loss of half of the fluid during the extraction procedure the final volume is corrected to compensate for the loss. Normally the final volume would be 1.6 mL. However, since one half the solution was discarded prior to finishing the extraction, one half the amount of target analyte(s), if present, is also discarded. To compensate, the final volume entered into the laboratory information management system is 3.2 mL.

6.4 The final extract solvent for all samples is acetonitrile. If some of the standards were in methanol, some problems may be introduced into the sample analysis. These may include but are not limited to peak broadening, retention time shift, and poor elution of peaks. By using the same solvent for standards and samples, these problems and others are kept to a minimum.

6.5 The pH of some batches may be lowered from the initial pH prior to extraction to prevent alkaline hydrolysis of several analytes. A weak acid such as acetic acid is used to lower the pH. The pH change is indicated on the extraction tracker.

NOTE: Step 6.5 is included at the suggestion of the Army Corps of Engineers (USACE).

7.0 SAFETY PRECAUTIONS AND WARNINGS

WARNING

ALL OF THESE COMPOUNDS ARE EITHER USED IN THE MANUFACTURE OF EXPLOSIVES OR ARE THE DEGRADATION PRODUCTS OF THE COMPOUNDS USED FOR THAT PURPOSE. WHEN MAKING STOCK SOLUTIONS FOR CALIBRATION, TREAT EACH COMPOUND WITH THE UTMOST CAUTION.

THIS METHOD IS RESTRICTED TO PERSONNEL EXPERIENCED WITH THE USE OF HPLC, SKILLED IN THE INTERPRETATION OF CHROMATOGRAMS, AND EXPERIENCED WITH EXPLOSIVE MATERIALS. WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

WARNING

STANDARD PRECAUTIONARY MEASURES USED FOR HANDLING OTHER ORGANIC COMPOUNDS SHOULD BE SUFFICIENT FOR THE SAFE HANDLING OF THE ANALYTES TARGETED BY THIS METHOD. THE ONLY EXTRA CAUTION THAT SHOULD BE TAKEN IS WHEN IT IS NECESSARY TO HANDLE NEAT MATERIAL OR IN THE RARE CASE OF HIGHLY CONTAMINATED SOIL SAMPLES.

WARNING

ALL SAMPLES MUST BE SCREENED PRIOR TO ANALYSIS. ANY SAMPLES WITH A CONCENTRATION ABOVE 1% TOTAL EXPLOSIVES WILL BE PULLED FROM THE SYSTEM AND HELD IN THE HPLC ROOM. THE PROJECT MANAGER, TEAM LEADER AND CLIENT WILL BE NOTIFIED. NO ACTION WILL BE TAKEN ON THE SAMPLE UNTIL A RESOLUTION AND SAFE HANDLING REQUIREMENTS ARE DETERMINED. IF NEEDED, GEL WILL SCREEN ALL SAMPLES ACCORDING TO APPENDIX 3

7.1 Wear eye protection with side shields while in the laboratory.

7.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client MSDS forms are also maintained.

7.3 Personal protective equipment

7.3.1 Gloves are required when handling the chemicals in this procedure. The gloves approved for this procedure are:

7.3.1.1 Nitrile gloves for concentrated acids and bases.

7.3.1.2 Latex gloves or equivalent will be worn at all times when handling any solvents or samples within the prep area.

7.3.1.3 For prolonged handling of solvents Chemi-Pro gloves should be worn.

7.3.1.3 For handling explosives with high concentrations (1 to 5%), leather gloves and face shield are required during the drying and grinding phase of the sample extraction.

7.3.1.4 For samples with high level explosives (greater then 5%) special instructions will be generated specifically for handling that sample and a copy retained with the data.

7.3.2 Work under a hood when using concentrated acids and bases.

7.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

7.4.1 Wear a plastic apron over lab coat when working with radioactive samples.

7.4.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

7.4.3 Prohibit admittance to immediate work area.

7.4.4 Post signs indicating radioactive samples are in the area.

7.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

7.4.6 Segregate radioactive wastes in radioactive waste containers provided by Waste Management.

7.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

7.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

7.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

7.6 Never leave gas cylinders unchained or untied, even when they are on the cylinder carts. The helium and air tanks should be replaced when pressure drops to ~500 psi.

7.7 The compounds of interest are considered fire and explosion hazards in their pure form. When diluted to less then 33% the primary hazard is the solvent, not the explosive material itself. If for any reason it is suspected that the explosives have recrystallized or particles of explosive exist in the sample, it will be treated as a pure explosive compound.

NOTE: The solvents used in the method are considered flammable and are handled in accordance with all MSDS sheets. The volume of solvents is minimized, but not to preclude performing routine analysis.

8.0 INTERFERENCES

8.1 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, under the conditions of the analysis, by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

8.2 Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

8.3 Interferences co-extracted from the sample will vary considerably from source to source. Although a general cleanup technique is provided as part of the method, individual samples may require additional cleanup approaches to achieve the sensitivity required.

8.4 The chromatographic conditions described allow for a unique resolution of the specific explosive compounds covered by this method. Other explosive compounds, in addition to matrix artifacts, may interfere.

8.5 During the liquid extraction process final concentration step, it is important that no salt be carried over from 100 mL volumetric to centrifuge tube. The salt will build up on the column causing erratic results and degrade the column.

9.0 APPARATUS AND MATERIALS; REAGENTS; EQUIPMENT AND INSTRUMENTS

9.1 General items:

9.1.1 Microliter syringes
9.1.2 2 mL amber vials with Teflon-lined septum and screw caps
9.1.3 Volumetric flasks: 1000 mL, 100 mL, 10 mL
9.1.4 Graduated cylinders: 2000 mL, 1000 mL, 250 mL, 100 mL, 25 mL, 10 mL
9.1.5 PTFE filters 0.45 µm or greater
9.1.6 5 mL and 10 mL syringes
9.1.7 25 mL Erlenmeyer flasks
9.1.8 20 mL Scintillation vials
9.1.9 40 mL amber vials
9.1.10 Magnetic stirring bars: 1000 mL and 100 mL size
9.1.11 Weigh boats, large and small capacity
9.1.12 125 mL sample bottles
9.1.13 Dropper bottle
9.1.14 Regular and Large capacity disposable pipettes
9.1.15 Concentrator tubes or equivalent
9.1.16 Sieves, 30 mesh

9.2 Chemicals: (Vendors listed are subject to change)

9.2.1 Acetonitrile HPLC grade or better (presently purchased from VWR)
9.2.2 Methanol HPLC grade or better (presently purchased from VWR)
9.2.3 NaCl , 12kg boxes (presently purchased from VWR)
9.2.4 8330 Standards (presently purchased from AccuStandard)
9.2.5 HPLC grade water or better
9.2.6 Surrogate: 1,2-Dinitrobenzene (presently purchased from AccuStandard)

9.2.7 Tetrabutylammonium hydroxide, 10% by weight or better (presently purchased from Aldrich)

9.2.8 8330 Standards (presently purchased from Supelco)

9.2.9 Sulfuric acid (presently purchased from Mallinckrodt)

9.2.10 Acetone HPLC grade or better (presently purchased from VWR)

9.3 Equipment:

9.3.1 Presently using a Agilent Technologies BDS 250 x 4.6 mm C-18 reverse phase column for primary analysis. Confirmation analysis is performed using a Phenomenex CN-5µg, 250 x 4.6 mm column.

9.3.2 Gradient pumping system HP model 1050 or 1100

9.3.3 Software capable of linear calculations

9.3.4 DAD HP model 1050 or equivalent

9.3.5 Ultrasonic sink with chiller

9.3.6 Magnetic stirring plate (heavy duty)

9.3.7 Vortex mixer

9.3.8 Organomation N-Evap apparatus

9.3.9 Drying oven without heat element

9.3.10 Computer, capable of running Windows-based programs and capable of controlling analytical instruments

NOTE: The apparatus listed above is the recommended instrumentation. The equipment listed is not all of the required equipment, but just a minimum needed to complete the analysis.

10.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

10.1 Samples must be collected in an amber glass bottle with a Teflon lined cap. The collection container must be washed with acetone and hexane rinsed, and dried before use in order to minimize contamination.

10.2 Samples must be protected from light and stored at 4° ±2°C after collection. All liquid samples have a holding date of seven days from the date of collection to the time of extraction. All solid samples have a holding date of 14 days from the date of collection to the time of extraction. Once extracted, the extract must be analyzed within forty days of the extraction date. However, during this period of time, the extracts should be kept refrigerated at 4° ±2°C in amber vials with Teflon lined screw caps. When holding dates are missed, the data should be flagged by the analyst and by the Quality Control department.

10.3 If the sample is outside of the holding time window, notify applicable project manager for guidance.

10.4 Sample holding times, addressed in Section 6.1 of Method 8330, are as follows:

10.4.1 Liquids are to be extracted within seven (7) days after sample collection.

10.4.2 Solids are to be extracted within fourteen (14) days after sample collection.

10.4.3 All samples are to be analyzed within forty (40) days after extraction.

11.0 SAMPLE PREPARATION TECHNIQUES

11.1 See Appendix 1 for the extraction of liquid explosive samples.

11.2 See Appendix 2 for the extraction of solid explosive samples.

12.0 PREPARATION OF STANDARDS SOLUTIONS AND QUALITY CONTROL STANDARDS

12.1 Standard Solutions:

12.1.1. Source standard solutions are prepared commercially by AccuStandard or other certified suppliers for Nitroaromatics and Nitramines. They are stored in a breakseal amber vial or equivalent in the refrigerator at 4°±2°C. They are replaced according to the expiration date designated on the vial by the vendor, or one year from the date of receipt, whichever time period is shorter.

12.1.2 Calibration Standards are prepared at a minimum of five concentration levels for each compound. They are prepared by diluting the stock solution with a 1:4 mixture of acidified DI water and Acetonitrile mixture. The concentration ranges for the calibration standards are found in ALPHA LIMS. See ALPHA LIMS for appropriate recipes for making all calibration and quality control samples.

12.1.3 Calibration check standard is a standard from a different source and/or lot than the calibration standards. It is used to verify that the instrument is calibrated correctly. The reading of the check standard must be within 85% - 115% of the initial calibration. The stock for the check standards is commercially prepared by an approved vendor. It should be stored in a Teflon-lined screw cap vial at 4°±2°C. The concentrations of the check standards should be prepared at the mid point of the curve. See ALPHA LIMS for current concentrations and recipe for preparing check standards. The calibration check standard is diluted with acidifed, DI water prior to analysis.

12.1.4 The surrogate, 1,2-dinitrobenzene, is made from AccuStandard M-8330-SS. The analyte is at 1000 µg/mL.

12.2 The source standards are received with certificates of analysis, which are maintained in Quality Systems. Upon arrival the source standard is given a unique identification number. The date received is written on the bottle and/or vial and initialed. The standard is then stored in the refrigerator at 4°±2°C until needed. See "Organic Standards Preparation and Traceability" (GL-OA-E-002) for explanation. The complete number is then logged into ALPHA LIMS. The supplier, concentration, lot number, date opened, date received, and expiration date must also be entered, if available. The standard should be checked for signs of evaporation before use. After the standard has been opened, it is only usable until the expiration date assigned by the vendor, or one year from the date of receipt, unless it shows signs of deterioration before this time period has elapsed.

12.3 When a standard is prepared, an identification number is assigned to that standard. If another standard is prepared by diluting the first, the diluted standard must also be given a unique identification number.

12.4 All standards are maintained in the explosion proof refrigerator, number 22.

12.5 Holding times of specific calibration standards are defined in Method 8330. More specifically, those working standards prepared with the addition of water in the final step are to be used the same day as prepared. An expiration date of 24 hours is used for these standards.

12.5.1 No specifically defined holding time is mentioned for intermediate standards above 1000 µg/L or working standards that do not include the addition of water in their recipe in Method 8330. General Engineering Laboratories assigns an

expiration date to these standards equal to but not exceeding the earliest expiration date of any Source Standard used to make one of these working standards.

12.5.2 Section 5.4.2 of Method 8330, Revision 0, September 1994, refers to the holding times of intermediate standards that cover the range of 2.5 - 1000 µg/L. Any intermediate standard falling within this range may be used for thirty days.

12.5.3 Expiration dates of standards are written on each standard's vial label and recorded in ALPHA LIMS.

12.6 Proper procedures for standard preparation are located in "Organic Standards Preparation and Traceability" (GL-OA-E-002).

13.0 INSTRUMENT CALIBRATION AND PERFORMANCE

13.1 Instrument setup and configuration.

13.1.1 Recommended system setup for primary analysis.

NOTE: This gradient is similar to one listed by Hewlett-Packard (see page 95 of reference 21.6), the manufacturer of the column currently in use in this lab.

13.1.1.1 Initial flow rate set to 1.0 mL/min with a gradient of 35% Methanol and 65% HPLC water. Gradient after this point is column dependent and will be generated upon installation of a new column. The general gradient is:

Time	% water	%MeOH
0	65	35
2	60	40
14	60	40
20	35	65
32	35	65
40	65	35

13.1.1.2 The DAD is programmed throughout the run cycle to shift monitoring wavelengths. Presently wavelengths 214, 224, 235, 254 and 264 are monitored and quantitated. With our present system we are capable of monitoring multiple signals. We have picked the above wavelengths due to their respective response factors.

13.1.1.3 We presently are injecting 100 µL. This volume is programmable and can be changed as necessary. Each time the injection volume is changed, the system must be recalibrated and new MDLs generated.

13.1.1.4 Recommended system set up for confirmation analysis:

Time	% water	%MeOH
0	65	35
6	65	35
30	30	70
35	65	30
40	65	35

13.1.1.5 Currently, confirmation analysis is performed using a cyano column with a six point calibration (50-20,000 ppb). Analytes are considered confirmed when the representative responses from the primary analysis and confirmation analysis are within the respective retention time window. Also, the confirmation analyte mass normally is

within a 30% difference from that of the primary analysis. However, due to matrix interference and coeluting peaks, analytes may be considered suspect and are qualified accordingly and narrated.

13.1.1.6 If an analyte is detected whose concentration differs between the primary and confirmation analysis by more than 40%, then the results are qualified as follows. In cases where both columns or detectors indicate an acceptable peak in the appropriate retention time window and the percent difference is greater than 40% but less than 70%, the analyte is reported as a positive result. Due to the high percent difference between the two columns, it is indicated as such on the appropriate Form I or Certificate of Analysis (CofA) with a P qualifier.

In cases where both columns or detectors indicate an acceptable peak in the appropriate retention time window and the percent difference is greater than 70%, the analyte may be reported as a positive result, depending on the client. Some clients, including DOE-AL, require that all results be reported, including those with percent difference values above 70%. These results are qualified with both a P qualifier and an X qualifier. In this case, the X qualifier denotes that the percent difference is greater than 70%. For all other clients, the analyte with a >70% difference is not reported.

13.1.1.7 Samples with responses for analytes on both columns or detectors that indicated an acceptable peak within the retention time window and an acceptable concentration match may be qualified with an X qualifier on the appropriate Form I or CofA if the analyst believes the hit is a false positive. The analyst may feel that the hit is the result of matrix interference or that the hit is another analyte altogether. If the X qualifier is used, it is explained in the case narrative.

13.1.1.8 The following analytes coelute on the cyano column: a)2,4,6-Trinitrotoluene, 2,4-Dinitrotoluene, and 2,6-Dinitrotoluene; b) 1,3,5-Trinitrobenzene and 1,3-Dinitrobenzene; b) m-,p- and o-Nitrotoluene.

13.1.1.9 The values reported are from the primary analysis. The confirmation analysis is used for qualitative purposes only.

13.2 An external standard technique is used to calibrate the instrument. Calibration is obtained by analyzing the standards using the same method used for sample analysis. Each standard must contain the same analytes, but at different concentration levels. The calibration standards must be run in random order. The area counts of each peak, in addition to the concentration of that particular analyte are used to plot a calibration curve. All calibration standards are automatically updated into the present method by performing an automatic calibration update. The correlation coefficient (r) for each compound of interest must be 0.995 or greater before the system can be considered calibrated. When the system is calibrated, a check standard prepared from a second source is used to verify the calibration. The analyte concentrations in this check must be within ±15% of the true concentration.

13.3 The HPLC^{3D} ChemStation is an instrument control, data acquisition and evaluation system for HP liquid chromatography instrumentation. The ChemStation and TARGET each offer the standard report calculations: ESTD, and ISTD. Quantification calibration features such as multiple level calibration, multiple signal calibration, multiple internal standards, multiple time reference peaks, and calibration bracketing

are available. Presently a linear calibration is used with the calibration curve forced through zero. ChemStation is used for instrument control and data acquisition. TARGET software is used to process, evaluate and store data.

13.4 Prior to analysis of samples

13.4.1 The HPLC system must be stabilized prior to use. This is checked by observing the pump pressure ripple is within -2% to 2% range. This value assures proper mixing and shows that all solvents have been degassed.

13.4.2 Before samples can be analyzed, the base line must be stable with little or no background noise. The UV lamp radiation level could take up to one hour to stabilize.

13.4.3 The continuing calibration check standard must pass ±15% of true value.

13.5 Samples containing target analyte concentrations that exceed the linear range of the analyte calibration curve must be diluted. The dilution level should be performed to place the highest analyte concentration between the middle and high points of the calibration curve (on column). If a sample is initially diluted and target analytes are not detected and non-target analytes are not interfering with the analysis, the sample must be reanalyzed at a lower dilution. Analysts should be aware that diluting samples will increase the detection limits for undetected analytes. Random dilutions without due cause are not acceptable.

13.6 A hard copy of the continuing calibration standard and runlog are maintained with each group of samples.

13.7 The calibration range for target analytes is currently 50 ng/ml to 20,000 ng/mL.

14.0 ANALYSIS AND INSTRUMENT OPERATION

14.1 Check standards and calibration standards are prepared as specified in current recipes. All standards are directly injected into the HPLC system by the auto sampler.

14.2 The run sequence is entered into the ChemStation software with the proper QC bracketing of each group of samples. Multiple injections from a sample vial are allowed. The following is a suggested sequence of QC and samples:

14.2.1 Instrument blank
14.2.2 Check standard
14.2.3 Method blank
14.2.4 LCS
14.2.5 LCS DUP
14.2.6 MS
14.2.7 MS Dup of 14.2.6
14.2.8 Parent sample of MS/MSD 14.2.6/14.2.7
14.2.9 Second sample
14.2.10 Third sample through fifth sample
14.2.11 Check standard
14.2.12 Sixth sample through fifteenth sample
14.2.13 Check standard
14.2.14 Repeat steps 14.2.11 through 14.2.13 for each additional 10 samples.
14.2.15 Always end sequence with a check standard
14.2.16 For batches of more than 20 samples repeat steps 14.2.2 through 14.2.14 as needed.

NOTE 1: Every analytical batch of 10 samples will be bracketed by the check standard. After every 10 samples another check standard is analyzed.

NOTE 2: At least daily, prior to analyzing samples, an instrument blank is run to verify the instrument and solvents used by the instrument are suitable for analysis.

NOTE 3: Instrument blanks are generally not analyzed on a routine basis prior to or following the check standard. Instrument blanks are only analyzed prior to a check standard if the samples are suspected to cause the check standard to fail due to interferences.

14.3 A runlog is generated daily for each group of samples analyzed, displaying which samples were analyzed and in what order they were analyzed.

14.4 General Operation of the HPLC System.

14.4.1 Allow system to warm-up for 15 minutes after turning on all pumps and detectors to allow instruments to be flushed thoroughly and the detector's internal temperatures to equalize.

14.4.2 Once the instrument has been allowed to warm up, purge each channel for approximately 5 to 10 minutes of any air bubbles that may be present. Then allow the instrument to equilibrate to operational pressure for a minimum of 15 minutes or 5 times column void time. Monitor pump pressure difference prior to starting analysis.

14.4.3 Verify column is preconditioned prior to starting the run sequence. A preconditioned column back pressure will be approximately 260 BAR.

14.4.4 If back pressure exceeds 350 BAR, column cleaning must be performed to prevent over pressurizing the system and possible column damage.

14.4.5 1 BAR equals 14.35 PSI.

14.5 System operation

14.5.1 Startup

14.5.1.1 Check all solvent containers and refill as necessary. Empty any waste containers that are greater then 3/4 full.

14.5.1.2 Check helium and air tanks. Replace if pressure is 500 psi or less.

14.5.1.3 Start system by selecting "System On" from the instrument sub menu.

14.5.1.4 Monitor pump pressure difference. When the difference is in the -2% to +2% range (usually stabilizes at +0.5%), system is ready to start analysis.

14.5.2 System shutdown: To shutdown the system, select "System Off" from instrument sub menu. This will turn off all pumps and detectors. For long shutdowns also turn off both helium and air tanks.

14.6 The HPLC system may be configured for up to a 250 µL injection. This can be changed through the instrument sub menu. The present method and MDLs are performed at a 100 uL injection volume. If the injection volume is changed, a new initial calibration must be run.

14.7 When running multiple samples:

14.7.1 Place all samples on sample tray (large external tray or smaller internal tray).

14.7.2 Verify run sequence against sample locations in the trays.

14.7.3 If performing a partial run in Sequence Table enter starting through ending sample to prevent possible overwriting of data. When starting a new sequence, this step is not required.

14.7.4 Start system by selecting "Run Sequence" from Run Control main menu.

14.8 System is designed for minimal maintenance. However, whenever repairs are required, consult manufacturer's technical manuals for guidance.

14.9 The data report will be client specific. The TARGET software is capable of generating custom reports based on the client's need.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Presently all maintenance is performed in accordance with Hewlett Packard technical manuals. All routine maintenance is also listed in the applicable technical manual.

16.0 DATA RECORDING, CALCULATION AND REDUCTION METHODS

16.1 All raw data files are magnetically backed up to the server; a computer print out is generated for the data review process. Sample data, runlogs and sequence logs are generated by the system before, during or after the instrument has completed the analysis. For each group of samples all data is placed in a folder and the batch number, date run and instrument will be placed on the front or tab. Also placed in the folder is a copy of the retention time window study for that day, prep data report, and a copy of any applicable nonconformance reports, and any other appropriate data.

16.2 The TARGET software is set up to calculate concentrations of sample extracts. When the raw data is entered into the laboratory information management system, a final data report is generated which will include all prep factors (but NOT a percent moisture for soils).

16.3 All records after completion of all reviews are filed in the HPLC cabinet for approximately 6 months and then maintained in accordance with GL-QS-E-008 for Management and Disposition of Quality Records.

16.4 The following calculations are used to generate sample results when using Method 8330:

16.4.1 Initial Calibration:

No calibration of response factors or calibration factors are necessary. Instead, a plot of peak area vs. concentration is made and the curve applied is a linear fit forced through zero.

16.4.2 Instrument Values:

$$y = mx$$

where:

y = area of target analyte detected
m = slope of line determined by initial calibration
x = concentration

16.4.3 Sample Result: (This calculation is performed by the laboratory information management system rather than the instrument software.)

$$SR = IV * PF * DF$$

where:

IV = Instrument value
PF = Preparation factor
PF_{solid} = (final extract weight/sample weight)
PF_{liquid} = (final extract volume/sample volume)
DF = Dilution factor
SR = Sample result

17.0 QUALITY CONTROL REQUIREMENTS

17.1 Before analysis of any samples the instrument must be calibrated, and all calibration curve correlation coefficients must be at or above 0.995. A second source calibration check standard is used to verify the calibration. Each day the second source calibration check standard must be analyzed and be within ±15% of the true value. A continuing calibration standard must be analyzed before and after each batch and after each group of 10 samples to verify calibration curve. This value must also be within ±15% of the true value. If at any time the standard fails, a second analysis is performed to verify first standard. If second standard also fails, the cause is investigated and corrected prior to running any additional samples. All samples not bracketed by good check standards are rerun to confirm the original data.

17.2 A method blank is used to determine background concentrations of analytes of interest that have potential to interfere with the sample analysis. These blanks are run with each batch of 20 or less samples. All analytes of interest must be below present PQLs to meet the quality control requirements.

17.3 A laboratory control sample and/or duplicate are run for each batch of 20 samples or less. The accuracy and precision of the extraction procedure may be monitored with these samples. Sample duplicate and sample spike may be used for this purpose.

17.3.1 If the percent recovery in the matrix or matrix spike duplicate falls outside the established SPC limits for recovery, the analyst should evaluate the LCS recoveries and method blank analyses. If the LCS and method blank analyses do not indicate a problem with the preparation procedures, the matrix spike recoveries may be attributed to matrix effect. Surrogate recovery data should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside the acceptance limits suggests more pervasive analytical problems then problems with the recoveries of either matrix spikes or surrogates alone. Analysts are not required to reanalyze the matrix spikes for failing recoveries, however, they should seek additional technical support before deciding not to reanalyze matrix spikes samples.

17.3.2 If matrix spike and duplicate recoveries are unacceptable, but the LCS recoveries meet current control limits, the matrix spike and Dup may be rerun to verify matrix interference.

17.3.3 The interference is reported with a text comment added explaining matrix interference, and a nonconformance is submitted.

17.3.4 If sample spike and duplicate and LCS recoveries are outside of the acceptable range, the entire batch is re-extracted and rerun.

17.3.5 Most DOE clients have contract requirements that mandate that the data must have a passing Laboratory Control Sample. If this is not met then the samples are re-extracted.

17.4 1,2-Dinitrobenzene (or other suitable surrogate) is added to all samples that undergo extraction. The surrogate is used to continuously monitor the sample extraction process. If the surrogate falls outside acceptable limits, a non-conformance report is submitted. That sample is re-extracted. If the surrogate recovery fails a second time, the failure is attributed to matrix interference. The data is reported with a text comment added to the data, and a non-conformance report is submitted.

17.5 A daily retention time window is generated from each check standard in an analytical sequence. These daily RT windows are determined from a previous retention time

study. See "Establishing Retention Time Windows for Gas Chromatographic Analysis" (GL-OA-E-001).

17.6 All detected responses found on the C- 18 column, below or above the PQL, will be confirmed by injection on a CN- column or equivalent. The primary quantitation will be derived from the C-18 column unless this is not in agreement with specific clients' requirements. When requested by certain clients (i.e., Navy), the reported value will be the lower concentration. The detection limit, however, will be the higher one. The spectral library may be used to further confirm the positive measurements.

17.7 NELAC certification requires a monthly analysis of the check standard to be performed at half the concentration and two times the concentration. This is used to verify the instrument is within calibration specification. Due to coelution and large concentration for 2-AM-DNT/4-AM-DNT and 2,4-DNT/2,6-DNT separate standards may be analyzed for the required two times the check standard verification.

18.0 DATA REVIEW, APPROVAL, AND TRANSMITTAL

18.1 After a sample batch has been run, data is collected and raw values are entered into the laboratory information management system. A data review check is then generated (placing the batch into the DREV status). The analyst places the case narrative data review sheet along with the prep sheet and all raw data into folder marked with the batch number, date run, and instrument used. After the analyst reviews the data and other folder contents, additional review is done by the group data reviewer or other qualified reviewer. The batch is then sent to 'Done'.

18.2 Analyst review - The analyst checks all chromatographs and checks the computerized calculation of the percent recoveries for the spike, duplicate, LCS's and all surrogates. The analyst then verifies that the check standards pass for the analytes of interest. If a target compound is detected on the C- 18 column, that compound is checked against retention time windows. If it is within the acceptable range, the detected analyte is confirmed on the CN column. This review is then placed in the folder with the other raw data. The analyst then initials the appropriate documentation and passes it on for the data validation review.

Both reviews are done independently. If the analyst detects a target concentration above the DAD calibration range, the sample is rerun at a suitable dilution.

18.3 Second level review - The Data Validator or other qualified reviewer assures that the concentrations that appear as raw data are entered correctly into the laboratory information management system. They will verify that check standards are within ±15% of true values and that the LCS, its duplicate and all surrogates are within acceptable ranges. The reviewer also checks date, time, dilution factors, and analyst initials against the data report. If everything is acceptable, the reviewer initials the documentation, and routes the data package to the appropriate person to send the package to "Done" in the system

18.4 An archived data package will have the following items: all chromatographs of the calibration check standards, method blank, LCS, LCS DUP, samples and sample spike and duplicate must be present. The batch sheet, sample batch sheet, prep data sheet, retention time window spreadsheet, and the data report must be present. The instrument method, calibration table, calibration curves, run log, and any other appropriate data are also included.

18.5 Proper technique for standard preparation is contained in "Organic Standards Preparation and Traceability" (GL-OA-E-002). In addition, after a recipe is entered into ALPHA LIMS, the calculations are checked and verified by a peer or equivalent.

19.0 RECORDS MANAGEMENT

19.1 All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

19.2 All Standards are recorded in ALPHA LIMS.

20.0 LABORATORY WASTE HANDLING AND DISPOSAL

Sample and reagent wastes are handled and disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

21.0 REFERENCES

21.1 Test Methods for Evaluating Solid Waste, EPA Manual SW-846, 3rd Edition. Method 8330, "Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)," Revision 0, September 1994.

21.2 Hewlett-Packard Series 1050 Auto Sampler

21.3 Hewlett-Packard Series 1050 Diode Array Detector

21.4 Hewlett-Packard Series 1050 HPLC System

21.5 Hewlett-Packard ChemStation software

21.6 HPLC for Environmental Analysis, Hewlett-Packard Publication Number 12-5091-9750E, (5/94).

21.7 TARGET Data Analysis Software.

21.8 Data Validation Standard Operating Procedures for CLP Routine Analytical Services. USEPA Region IV Science and Ecosystem Support Division of Quality Assurance Athens, Georgia, Revision 21, July 1999.

APPENDIX 1: EXTRACTION PROCEDURE FOR EXPLOSIVE LIQUID SAMPLES

Setup:

1. Calibrate open top balance.
2. Prepare saltwater by adding 325 grams NaCl to large beaker and then add 1000 mL. This solution is good for 30 days. OR, make daily by adding 243.75 grams NaCl to 750 mL of reagent water in a 1000 mL amber bottle.
3. Rinse all glassware with CH_3CN prior to use to prevent possible contamination.
4. Ensure sufficient spiking solution and surrogate is prepared prior to starting analyses.
5. Record all data on sample prep sheet for solid extraction.

Procedure:

1. Measure 251.3 grams NaCl and add to each 1000 mL volumetric flask. Place one large magnetic stirring bar in flask.
2. Measure 770 mL of sample into a glass graduated cylinder. For LCS or sample blanks measure 770 mL of grade A water.
3. Add an appropriate amount of surrogate to sample in volumetric flask to yield 250 ppb in 0.4 mL of extract.
4. Add an appropriate amount of spike to LCS, LCS Dup and matrix spikes if necessary matrix spike dup to the sample in volumetric flask to yield 500 ppb in 0.4 mL of extract.
5. Transfer 770 mL of sample to 1000 mL volumetric flask, bring magnetic stirrer to the maximum speed possible. (Position flask in best position on stirring plate.)
6. Stir sample until NaCl is TOTALLY dissolved.
7. Once NaCl is dissolved, add 160 mL of CH_3CN to sample while spinning by magnetic stirring. Add CH_3CN slowly to allow all entrapped air to escape and not overflow volumetric flask.
8. After CH_3CN has been added, allow sample to stir for a minimum of 15 minutes. Ensuring all CH_3CN is completely mixed into sample.
9. Turn off magnetic stirrer and wait 20 minutes for CH_3CN layer to develop at top of sample.
10. Transfer CH_3CN layer from 1000 mL volumetric flask to 100 mL volumetric flask. At this time a small amount of salt water will not affect the analysis.
11. Add 10 mL of CH_3CN to 1000 mL volumetric flask and repeat steps 8 through 10.
12. Add a small stirring bar to 100 mL volumetric flask. Then add 84 mL of saltwater to 100 mL volumetric flask. (325 g NaCl/L water.)
13. Stir volumetric flask for a minimum 15 minutes ensuring CH_3CN is completely mixed in with salt water.
14. Turn off stirrer and allow CH_3CN layer to develop for 20 minutes.
15. Transfer CH_3CN layer from 100 mL volumetric flask to graduated centrifuge tube, ensuring no salt water is transferred. A small amount of saltwater will produce a large solvent front degrading the sample chromatograph. Salt will also build up on the column shortening the column life and lessening column efficiency.
16. Add 1.0 mL of CH_3CN to 100 mL flask and repeat steps 13 through 15.

NOTE: If samples will not be analyzed immediately, STOP at this point until samples will be analyzed. Tetryl will slowly decompose in the presence of water; to prevent this, water is not added until just prior to sample analysis.

17. Place centrifuge tubes on N-evap apparatus and concentrate samples to 0.4 mL. DO NOT EVAPORATE SAMPLE TO DRYNESS. If sample is evaporated to apparent dryness, discard and re-extract.
18. Add 1.2 mL acidified DI water to centrifuge tube. Filter extract through 0.45 µm filter to remove any suspended particles.
19. Transfer extract to sample vial.
20. Place all glassware on cart, and place at glassware prep station.

APPENDIX 2: EXTRACTION PROCEDURE FOR EXPLOSIVE SOLID SAMPLES

Setup:

1. Calibrate open top balance.
2. Measure out 2 grams of building sand for each QC sample.
3. Prepare $CaCl_2$ using 5 grams per liter of DI water. This solution is used to remove -by coagulation- any clay that may be in the samples.
4. Rinse all glassware with CH_3CN prior to use to prevent possible contamination.
5. Assure sufficient spiking solution and surrogate is prepared prior to starting analyses.
6. Record all data on prep sheet.

Procedure:

1. If screening results indicate less than 1% contamination, then no special handling requirements are required. If sample screening results are 1% or greater special instructions are required before proceeding beyond this point.
2. Measure 5 to 10 grams of solid matrix into small plastic weighing tray and place in drying oven. Dry sample to apparent dryness in drying oven. This step may take several hours depending on liquid in the sample.
3. Sift sample through sieve (30 mesh). Transfer 2.0 grams of sample from sieve tray to scintillation vial.
4. Add an appropriate amount of surrogate to sample in scintillation vial to yield 250 ppb in 0.4 mL of extract.
5. Add an appropriate amount of spike to LCS, LCS Dup, matrix spike and, if necessary, matrix spike Dup to the sample in the scintillation vial to yield 500 ppb in 0.4 mL of extract.
6. Add enough CH_3CN to total 10 mL of liquid (surrogate, CH_3CN, and if appropriate, spiking solution) to each vial. Cap and gently stir to mix contents.
7. Mix sample on vortex mixer for 30 seconds or until sample is completely mixed with solvent which ever takes longer.
8. Place samples in vial rack in sonicator.
9. Turn on chiller unit and set temperature to be al least a minimum of 5 degrees less then room temperature. Turn on sonicator.
10. Place samples in sonicator and record date and time on prep sheet. Cover sonicator with cover. Sonicate for 18 hours.
11. After 18 hours in the sonicator, remove samples. If no other samples are to be sonicated, turn off chillier and sink. Let samples settle for 30 minutes. If there are more samples to be extracted, repeat steps 4 through 11.
12. Transfer 5 mL of sample from vial to centrifuge tube, filtering extract if extract is still cloudy after the 30 minute settling time.

NOTE: If samples will not be analyzed immediately, STOP at this point until samples will be analyzed. Tetryl will slowly decompose in the presence of water. To prevent this, water is not added until just prior to sample analysis.

13. Place centrifuge tubes on N-evap apparatus and evaporate samples to 0.4 mL. DO NOT EVAPORATE SAMPLES TO DRYNESS. If a sample is evaporated to apparent dryness, discard and re-extract.
14. Add 1.2 mL of acidified DI water. If the solution is cloudy from suspended clay, add instead 1.2 mL of $CaCl_2$ solution to remove any clay from suspension in the extract. All standards and samples will then need to be brought to volume with the $CaCl_2$ solution.
15. Transfer extract from centrifuge tube to HPLC micro vial, filtering extract through 0.45 μm filter to remove any suspended particles.

APPENDIX 3: SCREENING METHOD FOR METHOD EPA-8330

The following equipment (or equivalent) may be used:

125 mL wide mouth sample jars
Wooden spatulas
PTFE syringe filters, 0.45 µm, 25 mm
30 cc disposable syringes
Developer solution, 10w% Tetrabutylammonium hydroxide
Solution of known concentration, TNT standard
Acetone
Spec 20 spectrophotometer or equivalent
Balance, one place accuracy or greater
Vortex mixer
Waste container

SAMPLE EXTRACTION, PREPARATION AND ANALYSIS:

To ensure reproducible, qualitative results make sure the sample is homogeneous and, if a soil, contains <10% moisture.

A. Weigh out 10 ±0.1 grams or measure 10 ±0.1 mL into a sample bottle.
B. Add 50 mL of Acetone for soils, 40 mL of Acetone for waters, and 50 mL of Acetone for the known.
C. Mix with the vortex mixer for 30 seconds minimum or until the sample appears to be well mixed.
D. Let the sample settle for 5 minutes minimum.
E. Repeat steps A-D for each sample.
F. Repeat steps A-D with sand or DI water for a suitable blank.
G. To prepare a known solution, add 25 µL of 1000 ppm TNT solution to another appropriately prepared blank solution and proceed.
H. Using a 30 cc syringe, draw a 25 mL aliquot of the liquid.
I. Attach a syringe filter and dispense into the sample cuvette.
J. Obtain a background Absorbance reading at 540 nm ($Abs_{initial}$) and record it on the data logsheet.
K. Add one drop of developer solution and mix for 2-4 seconds.
L. Obtain a final Absorbance reading (Abs_{final}). Record it on the data logsheet.
M. Multiply the $Abs_{initial}$ by 4 and enter it into the formula:

$$TNT\ (ppm) = [Abs_{final} - (Abs_{initial} \times 4)] / (0.0323)$$ [1]

N. Record it on the data logsheet.
O. Repeat steps H-N for each sample.

SPECTROPHOTOMETER SETUP:

A. Energize the instrument for 30 minutes minimum.
B. Place selector switch on Transmission and zero the instrument.
C. Place the selector switch on absorbance.

REFERENCE:

A. TNT SOIL TEST SYSTEM, Ensys, Inc., RTP, NC

APPENDIX 4: EXPLOSIVES AND TNT DEGREDATION PRODUCTS
METHOD 8330

Explosives:

HMX	Bursting/High Explosives, Impurity in RDX manufacture
RDX	Bursting/High Explosives
Tetryl	Auxiliary Explosive ie, Initiators, Primers and Detonators
2,4,6-TNT	Auxiliary Explosive ie, Initiators, Primers and Detonators
PETN	Auxiliary Explosive ie, Initiators, Primers and Detonators

TNT Metabolites:

1,3,5-TNB	Photochemical decomposition product
1,3-DNB	Impurity in production grade TNT
NB	Reduction product
2-AM-4,6-DNT	Anaerobic biodegradation product
4-AM-2,6-DNT	Aerobic biodegradation product
2,4-DNT	Impurity in production grade TNT
2,6-DNT	Impurity in production grade TNT
2-NT	Reduction product
4-NT	Reduction product
3-NT	Reduction product

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

ACID DIGESTION OF TOTAL RECOVERABLE OR DISSOLVED METALS IN SURFACE AND GROUNDWATER SAMPLES FOR ANALYSIS BY ICP OR ICP-MS

(GL-MA-E-006 REVISION 8)

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1.0 STANDARD OPERATING PROCEDURE FOR ACID DIGESTION OF TOTAL RECOVERABLE OR DISSOLVED METALS IN SURFACE AND GROUNDWATER SAMPLES FOR ANALYSIS BY ICP OR ICP-MS

2.0 PURPOSE

To describe the manner in which surface and groundwater samples for Inductively Coupled Plasma (ICP) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis are digested by EPA SW-846 Method 3005A. Samples digested by this procedure are applicable for analysis by SW-846 methods.

3.0 DISCUSSION

This procedure deviates from Method 3005A as follows: sample and reagent volumes are half of the method recommendations.

3.1 Total Recoverable Metals - The entire sample is acidified with nitric acid at the time of collection. This sample is then refluxed with nitric acid and hydrochloric acid until the volume is reduced. The sample is diluted to a final volume, and then is ready for analysis.

3.2 Dissolved Metals - The sample is filtered at the time of collection. The liquid phase is acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested, as long as the acid concentration in the standards matches the acid concentration in the samples.

4.0 DEFINITIONS

4.1 Blank - Type I water that has been taken through the digestion process. The blank is used to determine the amount of background contamination.

4.2 Laboratory Control Sample (LCS) - A certified reference material that has been taken through the digestion process. The LCS is used to determine digestion accuracy and to determine if the digestion process is in control.

4.3 Laboratory Control Sample Duplicate (LCS DUP) - A duplicate of the LCS. The LCS DUP is used to determine reproducibility and to indicate precision.

4.4 Matrix Spike (MS) - A sample that has added to it a known amount of solution containing known concentrations of analytes. The MS is used to determine the presence or absence of interferences and matrix effects in the digested sample.

4.5 Matrix Spike Duplicate (MSD) - A duplicate of the MS. The MSD indicates reproducibility.

4.6 Sample Duplicate (DUP) – A duplicate of a sample. The DUP indicates reproducibility.

4.7 Type II water - Water that conforms to the following performance specifications:

Electrical resistivity, min.,	1.0
Total organic carbon, max., µg/L	50
Sodium, max., µg/L	5
Chlorides, max., µg/L	5
Total silica, max., µg/L	3

Type II water is dispensed throughout the laboratory through a centralized distribution system.

4.8 Type I water - Water that conforms to the following performance specifications:

Electrical resistivity, min.,	16.67
Total organic carbon, max., µg/L	100
Sodium, max., µg/L	1
Chlorides, max., µg/L	1
Total silica, max., µg/L	3

Type I water is dispensed within the metals prep lab by the "MilliQ" water system.

4.9 HNO_3 - Concentrated reagent grade 70.9% nitric acid.

4.10 HCl - Concentrated reagent grade 37% hydrochloric acid.

5.0 PROCEDURES

A batch consists of samples of the same matrix and quality control (QC) samples that are digested together. Each of the quality control samples listed in section 4.1 through 4.6 must be included in each batch at the frequency listed or as per client request. The blank, LCS and/or LCS DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent. The MS, MSD and/or DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent, or per specific client/program requirements.

5.1 Glassware preparation:

5.1.1 Glassware that has been cleaned according to "Glassware Preparation" (GL-LB-E-003) is soaked in a water and acid mixture for at least 30 minutes.

5.1.2 After soaking, the glassware is rinsed with copious quantities of Type II or Type I water, then inverted over clean, absorbent paper or onto a rack for drying.

5.2 Label Teflon beakers or centrifuge tube with the sample numbers in the batch.

5.3 Mix the sample to achieve homogeneity. Transfer a 50 mL aliquot of sample to the appropriately labeled beaker with a graduated cylinder. (If centrifuge tube is used, it must be calibrated before usage).

5.4 Quality control samples are prepared prior to digestion.

5.4.1 The beaker or tube to be used for the blank, MS, MSD and/or DUP, LCS and/or LCS DUP is labeled.

5.4.2 Unless otherwise noted, at least 50 mL of the sample is transferred to the MS, MSD and/or DUP beaker or tube.

5.4.3 Unless otherwise noted, 50 mL of Type I water is transferred to the LCS and/or LCS DUP beaker or tube.

5.4.4 The MS, MSD, LCS, and/or LCS DUP are spiked with known amounts of spiking solution.

5.4.5 The Teflon beaker or centrifuge tube to be used for the blank is labeled. 50 mL of Type I water is transferred to the beaker or tube. No spike or sample is added to the blank.

5.5 Sample digestion:

5.5.1 Add 1 mL of HNO_3 and 2.5 mL of HCl to the samples and quality control samples.

5.5.2 Cover the sample with a watchglass and heat the sample to 90 to 95° C until the sample volume is reduced to 7.5 to 10mL.

5.5.3 Do not allow the sample to go to dryness. Do not allow the sample to boil.

5.5.4 Remove the sample from the hot plate or block.

5.5.5 Allow the sample to cool.

5.5.6 If the sample contains particulate material that could clog the nebulizer, if necessary, you may filter or centrifuge the sample.

5.5.6.1 Be advised that filtration is a common cause of contamination. If a sample is filtered any QC associated with the sample must also be filtered. Additionally, if any sample in the batch is filtered the method blank and laboratory control sample must also be filtered.

5.5.7 Transfer the sample to a labeled centrifuge tube.

5.5.8 Dilute the sample to 50 mL with Type I water.

5.5.9 Cap the samples, organize them into a storage container, and label the storage container with the batch number of the sample group.

6.0 SAFETY, HEALTH AND ENVIRONMENTAL HAZARDS

WARNING

CONCENTRATED HCl AND HNO_3 ARE EXTREMELY CORROSIVE AND CAN CAUSE SEVERE BURNS TO THE SKIN

6.1 Wear eye protection with side shields while performing procedures in the laboratory.

6.2 All chemicals and samples should be treated as a potential health hazard and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client sample MSDSs are also maintained.

6.3 Personal protective equipment

6.3.1 Disposable gloves are worn and changed frequently when working with acids, glassware, or samples. Dirty gloves pose a contamination hazard to the samples. Gloves that have holes can be dangerous to the wearer by allowing acids and toxic metals to come in contact with the skin.

6.3.2 Hood doors are pulled down partially while digesting samples. Acidified samples can splash and pop as they are being heated.

6.3.3 To protect clothes and skin from being exposed to corrosive material, wear a lab jacket.

6.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

6.4.1 Wear plastic apron over lab coat when working with radioactive samples.

6.4.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

6.4.3 Prohibit admittance to immediate work area.

6.4.4 Post signs indicating radioactive samples are in the area.

6.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

6.4.6 Segregate radioactive wastes. Radioactive waste containers are obtained from the Waste Management.

6.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

6.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

6.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

6.6 In the event of an accident or medical emergency call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

6.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

7.0 RECORDS MANAGEMENT

7.1 Upon completion of batch preparation, digestion data shall be entered into the LIMS Prep Logbook (see Appendix 1) following the guidelines in GL-LB-E-008 for "Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms, and Other Record Keeping Devices."

7.2 Data to be entered into the logbook includes analyst name, prep data and time, initial volume or weight with units, and final volume with units.

7.3 Standards and reagents may also be entered into the logbook and fall under the guidelines of GL-LB-E-015 for "Control of Laboratory Standards," and GL-LB-E-007 for "Laboratory Standards Documentation."

7.4 Upon entry of prep data, obtain a printout of the logbook. The analyst listed on the logbook should sign and date the page near their printed initials. The logbook page is kept with the samples with which it is associated.

7.5 The entry of correct prep data is peer reviewed (correct dates, times, weights, volumes, SOP/revision, spikes, spike amounts and reagent information, etc.) Once data is reviewed, the batch is statused to DONE in LIMS, the logbook is signed and dated by the reviewer and the batch is ready for analysis.

7.6 Before a batch is to be peer reviewed, commit the analyst, date, time, initial volume, initial volume units, final volume, and final volume units into the Laboratory Information Management System.

8.1 LABORATORY WASTE

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

9.0 REFERENCES

9.1 Test Method for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Method 3005A, Revision 1, July 1992.

9.2 1992 Annual Book of ASTM Standards, D1193-91, "Standard Specification for Reagent Water"

APPENDIX 1: PREP LOGBOOK
(for illustrative purposes only)

Prep LogBook

Analyst: AJM
Batch: 30607
Prep Date: 07-FEB-2000 14:00
Lab SOP: GL-MA-E-013

Type	Sample Id	Lot. Id	Spike Amount	Spike Units
LCS	[illegible]	[illegible]	.25	mL
LCS	[illegible]	[illegible]	.25	mL
MS	[illegible]	[illegible]	.25	mL
MS	[illegible]	[illegible]	.25	mL
MSD	[illegible]	[illegible]	.25	mL
MSD	[illegible]	[illegible]	.25	mL

Type	Sample id	Parent Sample	Method	Initial Wt.	Final Volume	Prep Factor	Comments	Matrix
MB	[illegible]		[illegible] Full List Per QC	50mL	50mL	1		Water
SAMPLE	23-[illegible]		[illegible] Selenium	50mL	50mL	1		Waste Water
LCS	[illegible]		[illegible] Full List Per QC	50mL	50mL	1		Water
SAMPLE	23-[illegible]		[illegible] Selenium	50mL	50mL	1		Waste Water
SAMPLE	23-[illegible]		[illegible] Selenium	50mL	50mL	1		Waste Water
SAMPLE	23-[illegible]		[illegible] Selenium	50mL	50mL	1		Waste Water
SHELT	[illegible]	23-[illegible]	[illegible] Full List Per QC	50mL	50mL	1		Water
MSD	[illegible]	23-[illegible]	[illegible] Full List Per QC	50mL	50mL	1		Water
MS	[illegible]	23-[illegible]	[illegible] Full List Per QC	50mL	50mL	1		Water

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STANDARD OPERATING PROCEDURE

FOR

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

(GL-MA-E-009 REVISION 11)

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1.0 STANDARD OPERATING PROCEDURE FOR THE ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

2.0 PURPOSE

To describe the manner in which sediments, sludges and soils for Inductively Coupled Plasma (ICP) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis are digested by EPA SW-846 Method 3050B. Samples digested by this procedure are applicable for analysis by SW-846 methods.

3.0 DISCUSSION

A representative portion of sample is digested with nitric acid and hydrogen peroxide. This digestate is then refluxed with hydrochloric acid for ICP analysis only. This procedure deviates from Method 3050B in that sample volumes are half the method recommendations.

4.0 DEFINITIONS

4.1 Blank - Type I water that has been taken through the digestion process. The blank is used to determine the amount of background contamination.

4.2 Laboratory Control Sample (LCS) - A certified reference material that has been taken through the digestion process. The LCS is used to determine digestion accuracy and to determine if the digestion process is in control.

4.3 Laboratory Control Sample Duplicate (LCS DUP) - A duplicate of the LCS. The LCS DUP is used to determine reproducibility and to indicate precision.

4.4 Matrix Spike (MS) - A sample that has added to it a known amount of solution containing known concentrations of analytes. The MS is used to determine the presence or absence of interferences and matrix effects in the digested sample.

4.5 Matrix Spike Duplicate (MSD) - A duplicate of the MS. The MSD indicates reproducibility.

4.6 Sample Duplicate (DUP) - A duplicate of a sample. The DUP indicates reproducibility.

4.7 Type II water - Water that conforms to the following performance specifications:

Electrical resistivity, min.,	1.0
Total organic carbon, max., µ/L	50
Sodium, max., µg/L	5
Chlorides, max., µg/L	5
Total silica, max., µg/L	3

Type II water is dispensed throughout the laboratory through a centralized distribution system.

4.8 Type I water - Water that conforms to the following performance specifications:

Electrical resistivity, min.,	16.67
Total organic carbon, max., µg/L	100
Sodium, max., µg/L	1
Chlorides, max., µg/L	1
Total silica, max., µg/L	3

Type I water is dispensed within the metals prep lab by the "MilliQ" water system.

4.9 HNO_3 - Concentrated reagent grade 70.9% nitric acid.

4.10 HCl - Concentrated reagent grade 37% hydrochloric acid.

4.11 H_2O_2 - Concentrated 30% hydrogen peroxide.

5.0 PROCEDURES

A batch consists of samples of the same matrix and quality control (QC) samples that are digested together. Each of the quality control samples listed in section 4.1 through 4.6, must be included in each batch at the frequency listed or as per client request. The blank, LCS, and/or LCS DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent. The MS, MSD and/or DUP are digested at a frequency of one in 20 or per batch, whichever is more frequent, or per specified client/program requirements.

5.1 Glassware preparation:

5.1.1 Glassware that has been cleaned according to "Glassware Preparation" (GL-LB-E-003) is soaked in a water and acid mixture for at least 30 minutes.

5.1.2 After soaking, the glassware is rinsed with copious quantities of Type II or Type I water and then inverted over clean, absorbent paper or onto a rack for drying.

5.2 Label the Teflon beakers or centrifuge tube with the sample numbers in the batch. If centrifuge tube is to be used, it must be calibrated before usage. See SOP GL-LB-E-026 for centrifuge testing procedure.

5.3 Mix the sample to achieve homogeneity. Weigh approximately 0.5 grams of sample. Transfer the weighed sample to the appropriately labeled Teflon beaker or centrifuge tube.

5.3.1 Sample aliquots should not be taken from the top of an unmixed sample because large particles tend to rise in solid matrixes and heavy materials tend to sink in liquid matrixes.

5.3.2 Powdered samples may be homogenized by gently rocking the sample side to side. Then a representative aliquot may be taken from the center of the powder.

5.3.3 Other matrixes must be stirred, turned or mixed before sampling.

5.4 Quality control samples are prepared prior to digestion.

5.4.1 The beaker or tube to be used for the blank, MS, MSD and/or DUP, LCS, and/or LCS DUP is labeled.

5.4.2 Weigh approximately 0.5 of sample and transfer to the MS, MSD and/or DUP beaker or tube.

5.4.2.1 The MS, MSD, LCS and/or LCS Dup are spiked with known amounts of spiking solution.

5.4.3 Select a LCS. Mix the LCS to achieve homogeneity. Weigh approximately 0.5 of the sample and transfer to the LCS and/or LCS DUP Teflon beaker or centrifuge tube.

5.4.4 The blank beaker or tube is labeled and no water, spike, or sample is added to it.

5.5 Add 2.5 mL HNO_3 to the samples and quality control samples.

5.6 Gently swirl the sample acid mixture.

5.7 Cover the sample with a watch glass and heat the sample on a hot plate/block to near boiling. Reflux the sample for 10 to 15 minutes.

5.8 Remove the sample from the hot plate or block and allow the sample to cool.

5.9 Add 2.5 mL of concentrated HNO_3, replace the watch glass and reflux for 30 minutes.

5.10 Using a ribbed watchglass or vapor recovery system, allow the solution to evaporate to approximately 0.5 mL without boiling, or heat for 2 hours.

5.10.1 Remove the sample from the hot plate or block and allow the sample to cool.

5.11 Add 1.5 mL of H_2O_2 and 1.0 mL of Type I water. Return the sample to the hot plate or block and allow the peroxide reaction to occur. Continue to add H_2O_2 to the sample until the effervescence subsides. Do not add more than 5 mL H_2O_2.

5.11.1 Cover the sample with a ribbed watchglass, heating the acid-peroxide digestate until the volume is reduced to approximately 2.5 mL, or heat at 95° C ± 5° C without boiling for 1 hours.

5.12 If the sample is being prepared for ICP:

5.12.1 Remove the sample from the hot plate or block. Allow sample to cool.

5.12.2 Add 5 mL of concentrated HCl. Return the covered beaker or tube to the hot plate or block and reflux, without boiling, for 15 minutes.

5.12.3 Remove the sample from the hot plate/block.

5.12.4 Allow the sample to cool.

5.12.5 Dilute the sample to 50 mL with Type I water

5.12.6 Cap and shake the sample.

5.12.7 Organize the samples in a storage container and label the container with the batch number of the sample group.

5.13 If the sample is being prepared for ICP-MS analysis:

5.13.1 Do not allow the sample to go to dryness.

5.13.2 Remove the sample from the hot plate or block.

5.13.3 Allow the sample to cool.

5.13.4 Dilute the sample to 50 mL with Type I water.

5.13.5 Cap and shake the sample.

5.13.6 Filter each sample with a 2.0 µm pore size plunger type filter (PTF grade) or allow to settle overnight.

5.13.7 Organize the samples in a storage container and label the container with the batch number of the sample group.

5.14 If the sample contains particulate material that could clog the nebulizer, if necessary, you may filter or centrifuge the sample.

5.5.14.1 Be advised that filtration is a common cause of contamination. If a sample is filtered any QC associated with the sample must also be filtered. Additionally, if any sample in the batch is filtered the method blank and laboratory control sample must also be filtered.

6.0 SAFETY, HEALTH AND ENVIRONMENTAL HAZARDS

WARNING

CONCENTRATED HCl AND HNO_3 ARE EXTREMELY CORROSIVE AND CAN CAUSE SEVERE BURNS TO THE SKIN.

CONCENTRATED 30% H_2O_2 IS A VIOLENT OXIDIZER. KEEP AWAY FROM OPEN FLAMES AND RINSE WITH WATER IF SKIN CONTACT OCCURS.

6.1 Wear eye protection with side shields while performing procedures in the lab.

6.2 Treat all chemicals and samples as a potential health hazard and reduce exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals. A reference file of Material Safety Data Sheets (MSDS) and individual client sample MSDSs are also maintained.

6.3 Personal protective equipment

6.3.1 Disposable gloves are worn and changed frequently when working with acids, glassware, or samples. Dirty gloves pose a contamination hazard to the samples. Gloves that have holes can be dangerous to the wearer by allowing acids and toxic metals to come in contact with skin.

6.3.2 Hood doors are pulled down partially while digesting samples. Acidified samples can splash and pop as they are being heated.

6.3.3 To protect clothes and skin from exposure to corrosive material, wear a lab jacket.

6.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

6.4.1 Wear plastic apron over lab coat when working with radioactive samples.

6.4.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

6.4.3 Prohibit admittance to immediate work area.

6.4.4 Post signs indicating radioactive samples are in the area.

6.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

6.4.6 Segregate radioactive wastes. Radioactive waste containers are obtained from the Waste Management.

6.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

6.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

6.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

6.6 In the event of an accident or medical emergency call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

6.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

7.0 RECORDS MANAGEMENT

7.1 Upon completion of batch preparation, digestion data shall be entered into the LIMS Prep Logbook (see Appendix 1) following the guidelines in GL-LB-E-008 for "Basic Requirements for the Use and Maintenance of Laboratory Notebooks, Logbooks, Forms, and Other Record Keeping Devices."

7.2 Data to be entered into the logbook includes analyst name, prep data and time, initial volume or weight with units, and final volume with units.

7.3 Standards and reagents may also be entered into the logbook and fall under the guidelines of GL-LB-E-015 for "Control of Laboratory Standards," and GL-LB-E-007 for "Laboratory Standards Documentation."

7.4 Upon entry of prep data, obtain a printout of the logbook. The analyst listed on the logbook should sign and date the page near their printed initials. The logbook page is kept with the samples with which it is associated.

7.5 The entry of correct prep data is peer reviewed (correct dates, times, weights, volumes, SOP/revision, spikes, spike amounts and reagent information, etc.) Once data is reviewed, the batch is statused to DONE in LIMS, the logbook is signed and dated by the reviewer and the batch is ready for analysis.

8.1 LABORATORY WASTE

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

9.0 REFERENCES

9.1 Test Method for Evaluating Solid Waste; Laboratory Manual Physical/ Chemical Methods, Method 3050B, Revision 2, December 1996.

9.2 1992 Annual Book of ASTM Standards, Standard D1193-91, "Standard Specification for Reagent Water."

APPENDIX 1: SAMPLE PREP LOGBOOK

(for illustrative purposes only)

Prep Log Book

Analyst:	AJM
Batch:	[illegible]
Prep Date:	07-FEB-2000 14:00
Lab SOP:	GL-MA-E-013

Type	Sample Id	Lot Id	Spike Amount	Spike Units
LCS	[illegible]	[illegible]	.25	mL
LCS	[illegible]	[illegible]	.25	mL
MS	[illegible]	[illegible]	.25	mL
MS	[illegible]	[illegible]	.25	mL
MSD	[illegible]	[illegible]	.25	mL
MSD	[illegible]	[illegible]	.25	mL

Type	Sample Id	Parent Sample	Method	Initial Wt	Final Volume	Prep Factor	Comments	Matrix
MB	[illegible]		[illegible]	50mL	50mL	1		Water
SAMPLE	[illegible]		[illegible]	50mL	50mL	1		Water Water
LCS	[illegible]		[illegible]	50mL	50mL	1		Water
SAMPLE	[illegible]		[illegible]	50mL	50mL	1		Water Water
SAMPLE	[illegible]		[illegible]	50mL	50mL	1		Water Water
SAMPLE	[illegible]		[illegible]	50mL	50mL	1		Water Water
SDILT	[illegible]	[illegible]	[illegible]	50mL	50mL	1		Water
MSD	[illegible]	[illegible]	[illegible]	50mL	50mL	1		Water
MS	[illegible]	[illegible]	[illegible]	50mL	50mL	1		Water

[illegible] Page#_____

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

DETERMINATION OF METALS BY ICP

(GL-MA-E-013 REVISION 8)

APPLICABLE TO METHODS:
EPA Method 200.7,
EPA SW-846 Method 6010B,
and 200.7 CLP-M

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1.0 STANDARD OPERATING PROCEDURE FOR DETERMINATION OF METALS BY ICP

2.0 METHOD CODES

2.1 EPA SW-846 Method 6010B

2.2 EPA Method 200.7

2.3 EPA Method 200.7 CLP-M (modified Contract Laboratory Program)

2.4 Customer contract specifications.

3.0 METHOD OBJECTIVE AND PURPOSE

This standard operating procedure (SOP) describes the procedure for the determination of metals with Thermo Jarrell Ash (TJA) ICP-61E TRACE Spectrometer and the Perkin Elmer (PE) Optima Model 4300.

4.0 METHOD APPLICABILITY AND METHOD SUMMARY

4.1 Analytes: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, SiO2, Sn, Sr, Ti, Tl, U, V, Zn, P, and S.

4.2 Applicable Matrices: These methods are applicable to the determinations of any of the analytes listed above for various matrices including waters, oils, soils, sludges, Toxicity Characteristic Leachate Procedure (TCLP) extracts and other more unusual types of sample which are generally classified as a miscellaneous matrix.

4.3 General Method Summary: After samples are prepared in accordance with the sample preparation SOP, they are analyzed by Inductively Coupled Plasma (ICP) as follows:

4.3.1 The instrument is calibrated with a minimum of two calibration points for each element to be analyzed. The points consist of a calibration blank solution to define the lower calibration point and at least one standard calibration solution at the analyte concentrations to define the higher calibration point(s). A correlation coefficient of 0.995 or better is required for each analyte or the instrument is recalibrated for the analyte of interest.

4.3.2 Prepared client samples, check standards, and quality control samples identified in paragraph 21.1 are then analyzed. The check standards and quality control samples are used to determine the quality and acceptability of the analytical data.

4.3.3 Continuing Calibration Verification Samples (CCV) are analyzed a minimum of every 10 samples to ensure that the instrument is continuing to perform correctly.

5.0 METHOD SCOPE AND PERFORMANCE CHARACTERISTICS

5.1 Calibration Range: The calibration range consists of the concentrations between the calibration blank and that of the highest calibration standard for each analyte.

5.2 Tested Concentration Range: For ICP analyses, the upper limit of the linear range is determined by analyzing a linear range verification check standard, near the expected linear range limit. The analytically determined concentration of this standard shall be within ± 10% of the true value (± 5% for CLP).

5.3 Method Detection Limit studies for each analyte are performed or verified at least quarterly. These studies are conducted and calculated in accordance with SW-846, Chapter 1, Section 5.0, and "The Determination of Method Detection Limits" (GL-LB-E-001). The Reported Quantitation Limit (RQL) reflects the current MDL study. If reporting data by CLP protocol, an Instrumental Detection Limit (IDL) study is performed quarterly in accordance with USEPA CLP, Inorganic Statement of Work, ILM04.0.

5.4 Method Precision: To assure analytical precision of methods used, Laboratory Control Samples (LCS) and Laboratory Control Sample Duplicates (LCSD) are analyzed with each batch or as method requires.

5.5 Method Bias (Accuracy): Determined by calculating recoveries of LCS of a similar matrix.

6.0 REFERENCES

6.1 Perkin Elmer Optima 4300 Operator's Manual

6.2 Perkin Elmer Optima 4000 Series Hardware Guide

6.3 Thermo Jarrell Ash ICP-61E Trace Operators Manual

6.4 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1A, SW-846, 3rd edition, Nov. 1986. Method 6010B, "Inductively Coupled Plasma-Atomic Emission Spectroscopy", Rev 2, Sept. 1994. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

6.5 EPA Method 200.7, Revision 5.4

6.6 USEPA CLP, Inorganic Statement of Work, ILM04.0

7.0 INTERFERENCES TO THE METHOD

ICP analysis is subject to three types of interferences:

7.1 Physical interferences are those physical properties of a sample solution that prevent their introduction to the plasma with an efficiency equal to that of the calibration standards. This type of interference can be corrected via the bias correction calculation in SW-846, Chapter 1, Section 5.0; through the use of an internal standard, in accordance with the instrument operating manual; or by diluting the sample in reagent blank solution until the percent recovery is acceptable.

7.2 Chemical interferences are minimal in ICP Spectroscopy because the extremely high energy of the plasma breaks chemical bonds.

7.3 Interelement Spectral Interference can be overcome by use of Interelement Correction (IEC) factors.

8.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

8.1 Sample digestates are not extremely volatile or spontaneously combustible, but they are normally acidic and should be handled with care. Small spills may generally be wiped up with paper towels that can be disposed of in the trash. Larger spills may require the use of a mop. The mophead may have to be disposed of as potentially hazardous waste in accordance with the Laboratory Waste Management Plan, GL-LB-G-001. If the spilled digestates begin any obvious fuming or reacting, pour a generous amount of the acid neutralizer, located in each lab, onto the spill before attempting to clean it up.

8.1.1 Approved gloves will be worn to avoid skin contact with the digestate during clean-up.

8.1.2 Wear eye protection with side shields while performing procedures in the laboratory. An eyewash station is located in each analysis lab.

8.1.2 Do not persist in cleaning up a spill in the presence of strong fumes. Move out of the area, attempt to isolate the area, and notify your supervisor immediately.

8.2 These instruments use high voltage electricity and therefore should be shut completely down any time electronic components may be exposed to personnel or any liquids.

8.3 Prior to handling radioactive samples analysts must have radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

8.3.1 Protect counter tops with counter paper or work from radioactive sample handling trays.

8.3.2 Prohibit admittance to immediate work area.

8.3.3 Post signs indicating radioactive samples are in the area.

8.3.4 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

8.3.5 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

8.3.6 For additional guidance, see "Radioactive Material Handling," (GL-RAD-S-004), and the Laboratory Waste Management Plan, GL-LB-G-001.

8.4 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). Individual sample MSDS forms provided by the clients are also maintained.

8.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

8.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

8.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

8.6 Never leave gas cylinders unchained or untied, even when they are on moving carts.

8.7 In the event of an accident or medical emergency call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

8.8 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

9.0 CAUTION WARNINGS

Special care should be taken when handling HF to ensure that the acid does not come into contact with the skin.

10.0 APPARATUS AND MATERIALS; REAGENTS; EQUIPMENT AND INSTRUMENTS

10.1 Ancillary Equipment

10.1.1 Replacement glass parts for the ICP such as quartz torch bodies, purge extension windows, injector tips, nebulizers and spray chambers may be ordered from an approved vendor through GEL's Purchasing Agent.

10.1.2 High purity Argon and Nitrogen Gases are provided to the ICP instruments, via a network of pipelines, into the lab from liquid storage tanks located outside the building. The argon and nitrogen are purchased from a GEL approved vendor.

10.1.3 Consumable materials such as tubing are often attainable from various scientific product companies. The GEL Purchasing Agent can help to find the best prices from an approved vendor. All orders are placed through GEL's Purchasing Agent.

10.2 Reagents, Chemicals, and Standards

10.2.1 Reagents: Reagent grade and ultrapure acids (HNO_3, HCl), 5% or 1% Li solutions, 1000 ug/ml Scandium solution, 5% Cesium, and 1000 ug/ml Yttrium solution.

10.2.2 Standards: See "Metals Standards" (GL-MA-E-004).

10.2.3 Other Chemicals: Additional compounds, surfactants, oils, cleaning agents, etc. may be routinely ordered through GEL's Purchasing Agent.

10.3 Instrumentation

10.3.1 TJA ICAP 61E Trace with IBM compatible PC and printer

10.3.2 PE Optima 4300 with compatible PC and printer

10.3.3 TJA Autosampler

10.3.4 Optima Autosampler

10.3.5 Polyscience6105 PE Chiller

10.3.6 Appropriate Nebulizer (i.e., Meinhard or Burgener Mira Mist)

10.3.7 Refrigerated recirculating bath for Trace ICP

11.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

11.1 Aqueous samples should be preserved with HNO_3 to a pH of < 2 prior to receipt by the analyst. Sediment samples should be kept at 4°C ±2° prior to analysis.

11.2 See "Sample Receipt, Login, and Storage" (GL-SR-E-001).

12.0 SAMPLE PREPARATION TECHNIQUES

12.1 All samples, except drinking water with Turbidity <1 NTU and samples specifically exempted by contract, are prepared in accordance with the SOPs for Metals Digestion: GL-MA-E-006 (USEPA SW-846 Method 3005A), GL-MA-E-008 (USEPA SW-846 Method 3010A), GL-MA-E-009 (USEPA SW-846 Method 3050A), GL-MA-E-015 (USEPA SW-846 Method 3051), and GL-MA-E-012 (CLP Method ILM04.0). Other digestion procedures may also be used.

12.2 Additional filtration may be required to prevent clogging of sample introduction system.

12.3 Sample spills should be handled as stated in Section 8.1.

13.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Routine Preventative and Special Operational (Failure)

13.1 Routine Preventative Maintenance (PM) is recommended as follows:

Frequency	Procedure
When Needed	Oil the peristaltic pump with silicon spray Replace peripump sample introduction tubing Change pump hoses on drain systems Check drain waste collection containers and empty as needed Clean/replace nebulizer Clean/replace torch. Align according to manufacturer's specifications Clean/replace air filters

13.2 Non-Routine Maintenance Procedures (Special, Operational or Failure Mode Maintenance)

13.2.1 If the instrument will not function properly see the trouble shooting section in the appropriate operator's manual.

13.2.2 If the analyst is unable to fix the instrument, call the GEL Instrument Technician, and if needed, the manufacturer's Service Department.

13.3 See ICP Maintenance Logbook for routine records. Preventative maintenance and service should be recorded in the maintenance logbook.

14.0 PREPARATION OF STANDARD SOLUTION AND QUALITY CONTROL SAMPLES

14.1 Source standards records are recorded in the Metals Source Standards Logbook, which is maintained in the Metals laboratory. The preparation of working standards is fully described in the "Maintain Reference Materials" application in ALPHA LIMS.

14.2 Standards are receipted, labeled, prepared and stored in accordance with GL-LB-E-007 for Laboratory Standards Documentation and GL-LB-E-015 for Control of Laboratory Standards.

15.0 INSTRUMENT CALIBRATION

15.1 Calibration and sample analysis are conducted automatically using the autosampler. (Samples can also be analyzed manually.)

15.1.1 Profiling: All analytical channels were aligned within specifications during initial installation or realigned after relocation of the instrument by profiling daily, all elements will be peak-on-center. Profiling should be done after plasma warm-up prior to sample analysis and verified routinely during the day (more frequently on days with high temperature and humidity fluctuations).

15.1.1.1 Operate/Profile instrument using the procedures found in the corresponding ICP Operator's or Hardware Manual.

15.1.1.2 On the TJA Trace ICP, the profile spectrum shift position should fall within +/- 0.1 spectrum shift units. If the profile exceeds this range, recalculate the new spectrum shift position. Repeat the recommended profiling procedure as necessary to attain the +/- 0.1 spectrum shift specification.

15.1.1.3 The PE Optima 4300 is autoprofiled using an Hg lamp.

15.1.1.4 When an acceptable profile is attained, print the graphical profile and display and record the profile data in the appropriate profile logbook.

15.1.2 Standardization: Standardization is required every twenty-four hours in which the instrument will be used. Additionally, restandardization and/or recalibration is required when calibration checks fail.

15.2 Calculations are described in the instrument manuals.

15.3 Calibration standards may vary according to method. A minimum of a blank and standard are required, but a typical calibration uses a blank and three standards of varying concentration. For the multiple standard curve, the correlation coefficient (R) must be equal to or greater than 0.995.

15.4 For typical (recommended) calibration standards refer to Appendix 2.

15.5 For continuing calibration requirements see Section 21.

15.6 For actions concerning a calibration verification failing to meet requirements, see Section 21.3.

16.0 INSTRUMENT PERFORMANCE REQUIREMENTS

16.1 Before samples may be analyzed the instrument must be calibrated and verified using a calibration standard readback analyses (for CLP only), an Initial Calibration Verification (ICV) which is prepared from an independent source, an Initial Calibration Blank (ICB), Interference Check Sample(s) (ICS-A, ICS-AB) and Practical Quantitation Limit (PQL or CRI). These must meet the requirements stated in Section 21.2 for each analyte being reported, unless specified otherwise by the client or contract.

16.2 The instrument calibration and all continuing verification data is maintained on the printed hard copy and electronically saved onto the computer network. The printouts are kept in chronological order by instrument. Recent files are stored in the respective metals laboratories and older records are archived in the warehouse.

17.0 ANALYST AND METHOD VERIFICATION REQUIREMENTS

17.1 Analyst training is conducted in accordance with "Employee Training" (GL-HR-E-002).

17.2 Method performance is verified by the conductance of MDL studies in accordance with the "The Determination of Method Detection Limits" (GL-LB-E-001), and by the evaluation of laboratory proficiency samples (audits).

18.0 ANALYSIS PROCEDURES AND INSTRUMENTAL OPERATION

18.1 All samples are introduced to the instrument via a peristaltic pump. The amount of sample entering the instrument is dependent on the pump speed, the diameter of the pump tubing, and the nebulizer efficiency.

18.2 Run Sequence

18.2.1 Calibration sequence (may vary slightly under different autosampler files/see Appendix 2 also).

S0	(reagent blank-3% HCl/1%HNO_3)
S0.1	(100 ppb standard)
S0.5	(500 ppb standard)
SCAL	(1000 ppb standard)
S10	(20-50 ppm standard)

18.2.2 The calibration verification steps include:

Calibration Standard Readbacks (required for CLP only)
ICV
ICB
PQL (required for 6010B)
CRI (required for CLP)
ICS-A
ICS-AB
CCV (required for CLP prior to sample analysis)
CCB (required for CLP prior to sample analysis)

18.2.3 Samples (10 samples or less)

18.2.4 Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB)

18.2.5 Repeat steps 18.2.3 and 18.2.4 through the end of the run or until applicable verification is out of specifications.

18.2.6 Final verification steps in order:

CRI (required for CLP only)
ICS-A (required for CLP only)
ICS-AB (required for CLP only)
CCV
CCB

18.3 For data storage see section 24.1.

18.4 General operation of the instrument

18.4.1 The Thermo Jarrell Ash 61E TRACE is a simultaneous axial inductively coupled argon plasma emission spectrometer. As configured for General Engineering Laboratories, LLC, it is capable of analyzing 32 elements: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, SiO2, Sr, Ti, Sn, Tl, U, V, and Zn. The operating software of the system is a menu driven type.

18.4.2 The Perkin Elmer Optima 4300 is a simultaneous, dual view, inductively coupled, argon plasma emission spectrometer. As configured for General Engineering Laboratories, LLC, it is capable of analyzing 33 elements: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, SiO2, Sr, Ti, Sn, Tl, U, V, and Zn. The operating software of the system is a menu driven type.

18.4.3 Typical Analysis Problems

18.4.3.1 Sample Overrange: If an analyte is saturated for a sample, even if this element is not required, it is advisable to dilute the sample to an acceptable range and rerun, especially if the saturated element is an interferant on an analyte. Dilutions are required if the value of an analyte exceeds 100% of the working linear range when the element of interest is being reported, or is interfering with an element that will be reported. Dilution factors must be taken into account when reporting final values. Additionally, further rinse and/or an acidified rinse solution may be required before continuing with the next sample.

18.4.3.2 Torch/Sample Introduction Drift: Various changes in torch plasma conditions, sample introduction, or other external factors can have a great effect on the analysis.

- If sample introduction drift is suspected several items should be reviewed. Check the peristaltic pump tubing for wear and replace as needed. Check the internal standard to make sure it is being introduced to the instrument at a constant rate. Check the nebulizer to ensure that it's free of clogs and that the spray is a continuous mist.
- Profile drift may mimic torch/sample introduction drift. Reprofiling should be done routinely. Profile drift is a function of temperature and should be checked more frequently when large temperature swings are observed. During an analytical run profile drift is evident when a clean blank shows significant deviation from zero. As suggested by the manufacturer, two elements to track for this problem are Na and Al.

- Tubing connections may become loose, allowing air to bubble into the sample path. Tighten or replace tubing connection as necessary.

18.5 Power switches and auxiliaries are addressed in detail in the appropriate operator's manual and/or hardware guide.

18.6 Start-up and shutdown procedures are addressed in detail in the appropriate operator's manual and/or hardware guide.

18.7 Sample quantity requirements vary based on several different factors such as nebulizer type, diameter of tubing, and pump rate.

18.8 Autosampler can be used with various nebulizers by attaching the sample introduction tube to the autosampler sample tube. The autosampler rinse should be setup by connecting the autosampler rinse tubing to the peristaltic pump in the instrument.

19.0 CALCULATIONS AND DATA REDUCTION METHODS

19.1 Any dilutions, concentrations, or preparation factors must be taken into account prior to reporting data to a client. The appropriate factors are entered into LIMS.

19.2 Care must be taken that the correct units are being employed. Analytical results originating from the 61E TRACE/Optima are reported in ppb or µg/L.

20.0 DATA RECORDING

20.1 The 61-E TRACE data is generally stored on the network as a database file named SAMPLES.DBF and printed at the instrument as each sample is analyzed. The Optima 4300 is stored on the Network as a CSV file.

20.2 ICP samples and standards are generally analyzed in three replicates (minimum of 2) and the reported value is the average of the replicates. At times one replicate may be removed due to an attributable cause. This attributable cause should be documented on the hard data (i.e. third replicate ran out of volume). The average of the two remaining replicates are subsequently recalculated prior to reporting the data to the client. The data for individual replicates is printed on the hard data along with the average, but only the average of the replicates is typically stored in the Trace computer.

20.3 Data is retrieved by the data entry personnel where unused data can be eliminated, dilution factors entered, and conversions made prior to uploading to the Laboratory Information Management System (ALPHALIMS).

21.0 QUALITY CONTROL REQUIREMENTS

21.1 Frequency of Quality Control Activities (see Appendix 3)

21.1.1 The SCAL and S10 are analyzed immediately following the calibration. These analyses are sometimes called calibration standard readbacks. This step only applies to CLP analyses.

21.1.2 The Initial Calibration Verification (ICV) is performed following each calibration. The Continuing Calibration Verification (CCV) is performed following every ten or less samples. For CLP analysis the ICV is performed immediately following calibration. For CLP analyses the CCV is run prior to the analysis of any samples and follows every ten or less samples. Any quality control samples excluding the CCV and CCB are counted as samples. Therefore, a CLP analytical run should end with a final CCV and CCB. Additionally, no more than two hours should pass between analyzing successive CCV's that bracket reportable data.

21.1.3 An Initial Calibration Blank (ICB) is performed immediately following the ICV and Continuing Calibration Blanks (CCB) must follow each CCV.

21.1.4 The PQL standard is analyzed after each calibration. This standard may also be labeled as a CRDL standard. For CLP work, the CRI is analyzed at the beginning and at the end of each analytical run, and at a minimum of two times per eight hours. For CLP analyses the CRI is analyzed at two times the CRDL or two times the IDL, whichever is greater.

21.1.5 An Interference Check Standard is analyzed after the calibration. For CLP analysis, an ICSA and ICSAB must be performed before the final CCV, CCB.

21.1.6 A method blank is performed for each batch of twenty or fewer samples, or more frequently per client contract requirement. For CLP analyses, the requirement is one method blank per up to twenty samples in an SDG.

21.1.7 A matrix spike (MS) and a sample duplicate (DUP), or a matrix spike and a matrix spike duplicate (MSD) are analyzed for each batch of 20 or fewer samples or per client or method requirements. For a matrix spike recovery to be applicable the sample value may not exceed four times the nominal concentration of the spike. For CLP analyses, the requirement is one MS/MSD or MS/DUP per up to twenty samples in an SDG.

21.1.8 A laboratory control sample (LCS) is normally analyzed with each batch of twenty or fewer samples. An LCS Duplicate (LCS Dup) is performed at the same frequency as the LCS when required by a specific program or client.

21.1.9 Serial dilutions are analyzed to indicate the presence or absence of interferences. The analyte concentrations must be greater than 50 times the detection limit for a serial dilution to be applicable. The serial dilution is generally performed at a 5 x dilution of the test sample.

21.1.10 When performing CLP analyses, a serial dilution will be performed for each SDG of up to twenty samples.

21.1.11 When performing CLP analyses, a post-spike must be performed on the original sample when the matrix spike recovery falls outside the control limits and the sample result does not exceed 4x the spike added. Spike the unspiked aliquot of the sample at 2x the indigenous level or 2x the CRDL, whichever is greater. Post-spike analysis is not required for Ag.

21.2 Acceptance Limits (see Appendix 4)

21.2.1 For CLP (ILMO) methods, the calibration standard readbacks must fall between 95% and 105% of the true value. If data is to be reported by CLP, a linear range verification check standard shall be performed and reported quarterly. The linear range standard shall be run during a routine analysis and the determined concentration shall fall within 5% of the true value.

21.2.2 ICV and CCV results must fall between 90% to 110% of the true values for work under EPA SW-846 Method 6010B. ICV must be between 95% to 105% of the true value for work under EPA Method 200.7 and USEPA CLP Method 200.7 CLP-M.

NOTE: The ICV is a second source standard and may be used as the CCV as it also will show calibration verification.

21.2.3 For CLP, the ICB and CCB results must have an absolute value less than or equal to the PQL results. For SW-846, the results of the calibration blanks must agree within three standard deviations of the mean blank value. If not, repeat

the analysis two more times and average the results. If the average is not within three standard deviations, terminate the analysis and correct the problem.

21.2.4 The PQL should fall within 70% to 130% of the accepted value. For CLP analysis no specific acceptance criteria have been established for the CRI, however an unofficial range of 50% to 150% has been set for guidance purposes. For CLP the CRI is exempted for Al, Ba, Ca, Fe, Na, and K.

21.2.5 The analytes for the ICS-AB results must fall between 80% and 120% of the true value. The analytes for the ICS-A must have an absolute value +/- 2 times the CRDL.

21.2.6 Method blank results should fall less than the RDL but no less than twice the negative RDL. Additionally, the method blank may exceed the RDL provided that the blank value is insignificant relative to the lowest value of the samples in the batch. Specifically, the blank value must fall less than 10 times the lowest value of the samples in the batch. For CLP analyses, the method blank must have an absolute value less than the CRDL or less than 10 times the lowest value of the samples in the batch. All failures must be reprepped.

21.2.7 Matrix spike and matrix spike duplicates recoveries should fall between 75% and 125% or per client contract. Matrix spike recoveries are applicable to those sample values that do not exceed four times the nominal concentration of the spike. Recoveries of one or more of the matrix spikes that fall outside recommended ranges may indicate an improper sample digestion, sample inhomogenity, or matrix interference. The LCS and LCS DUP are therefore used for indicators of sample digestion validity.

21.2.8 LCS and LCS DUP recoveries and RPD's must fall within process control limits as established by Statistical Process Control, manufacturer's certification, or method requirements.

21.2.9 Serial dilution results that agree within 10% of an initial raw value greater than 50 times the IDL suggest the absence of interference. Failures of a serial dilution should be noted, but are not considered pass/fail criteria.

21.2.10 The relative percent difference (RPD) between an MS and MSD or a sample and DUP should falls within ± 20% if the analyte level is sufficiently high (5x the CRDL for CLP analyses).

21.3 Out of Control situations

21.3.1 ICV and or CCV failure requires a recalibration of the instrument and/or repreparation of standard solutions. Samples bracketed by calibration verifications that are not acceptable for required analytes must be reanalyzed. An ICV or CCV that has failed may be rerun provided there is an attributable cause known to have affected the check standard only and not the previous samples. Examples of an acceptable cause may be a sample tip out of solution during analysis, an incorrectly prepared CCV, or obvious carryover in the CCV from a very high sample immediately prior to the CCV. If a CCV is reanalyzed, the data must be lined through, initialed and dated, and the reason for the rerun must be documented on the raw data. In addition, corrective action should be taken to eliminate the cause of the initial CCV failure to prevent future occurrence.

21.3.2 ICB and CCB failure requires reblanking or recalibration of the instrument and/or repreparation of the calibration blank. When analyzing under SW-846,

a CCB may be accepted above the RQL level under two conditions: 1) the CCB is acceptable if the sample value is below the RQL and 2) the CCB is acceptable if the level of analyte in the CCB is less than 1/10 the analyte value in the lowest reported sample.

21.3.3 ICS failure requires that the interferences be corrected, via recalculation, of Interelement Correction Factors or selection of background correction factors so that the ICS can be read within the required limits before samples are analyzed. ICS failure at the end of an analysis period will require that the samples run for the affected analyte(s) during that period to be reanalyzed. For CLP analyses, in the event of an ICS failure, terminate the analysis, correct the problem, recalibrate the instrument, and reanalyze the analytical samples analyzed since the last good ICS.

21.3.4 Calibration standard readback failure requires that the instrument be recalibrated (for CLP only).

21.3.5 PQL failure should be evaluated, but no action is required if the results are outside of the 70% to 130% range (50-150% for CLP).

21.3.6 Matrix spikes, duplicates and spike duplicates are used only as indicators of method effectiveness on that sample and will not be used as acceptability criteria for the process, unless it a special requirement of the client. For CLP analysis, matrix spikes and duplicates that are outside the acceptance criteria will be flagged according to the ILMO4.0 Inorganic Statement of Work. Post spikes are performed for the analytes in which matrix spikes or spike duplicates are outside the acceptance criteria. Exception is given to Ag.

21.3.7 LCS and/or LCS duplicate results outside of established acceptance limits require the batch to be redigested and reanalyzed.

21.3.8 When analytical results suggest the presence of interference, one of the methods listed in section 18.4.3.1 must be employed. For CLP analyses, serial dilutions that suggest the presence of interference per Section 21.1.9 are flagged according to the ILM04.0 Inorganic Statement of Work E-24 Section

21.3.9 The number of counts and percent RSD of the internal standard are monitored per sample. However, there is no acceptance criteria per SW 846 and ILMO methodology. The internal standard can serve as a guide for troubleshooting instrument and/or sample problems.

21.4 Analytical data is evaluated for conformance with the requirements stated in Section 21.2 by the analyst during and/or after the analysis, but before the data is entered into the LIMS. Data may be accepted or rejected by the analyst at this point or by the data reviewer(s) as stated in Section 22.

21.5 Corrective actions taken for data not conforming to the requirements in Section 21.2 are stated in Section 21.3. If these corrective actions can be taken by the analyst prior to the acceptance of the data, then no nonconformance documentation is required. However, if these corrective actions include redigestion of the batch or sample, if the data has already been accepted, or if the corrective action requires an instrument service call, then a nonconformance/ corrective action report should be completed. This report includes the date, person requesting the action, sample(s) or batch(es) affected and action requested, all provided by the requester. The person taking the action will provide any pertinent comments and their signature and date the action is completed. The disposition of the nonconformance will then be verified by the group leader and QA officer if pertinent. These reports will be kept on file. See

"Documentation of Nonconformance Reporting and Dispositioning, and Control of Nonconforming Items" (GL-QS-E-004).

22.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

22.1 The LIMS Data Report and the original batch sheet are provided to the ICP reviewer.

22.2 A knowledgeable person other than the originating analyst shall review the data within the day or specified time limit. When this review is completed and all of the data is found to be acceptable, the reviewer signs and dates the batch data report. If the reviewer determines that the reviewed data is not acceptable and requires additional work or correction, it is returned to the group leader or representative with an appropriate explanation.

22.3 Listed below are the data review responsibilities at the Analyst, Peer Review and Validator levels:

22.3.1 Analyst Review is performed by the analyst who generated the data before the data is submitted for entry into the LIMS. The analyst uploads the data to ALPHALIMS and completes the batch data report.

22.3.2 Peer Analyst Review is performed by an individual who did not perform the analysis but is familiar with the analytical method used and the reporting requirements. This person reviews the complete data report after all data is entered and ensures that any data entry corrections are made before it is approved, and then signs the batch data report. If the data does not meet the necessary quality requirements and needs further analysis, it is returned to the analyst

22.3.3 Data Validation: For data requiring forms packages, the forms are generated per contract requirements and validated per GL-MA-E-017.

22.4 Specific items that are reviewed at each level include the following:

22.4.1 Analyst Review: Before data is submitted for entry into LIMS.

22.4.1.1 All analyses in the batch are completed with explanations of exceptions.

22.4.1.2 Any corrections and comments on the data are properly initialed and dated.

22.4.1.3 Proper standard identification numbers appear on the runlog to ensure Traceability from the data to original source standards.

22.4.1.4 Data acceptance limit criteria identified in Section 21.2 are met or an explanation given.

22.4.2 Peer Analyst Review before Data is statused to DONE in ALPHALIMS:

22.4.2.1 All data is complete and accurate in the LIMS Data Report.

22.4.2.2 Any exceptions or shortcomings have been sufficiently explained or corrected.

22.4.2.3 Data is reported in the proper units or an explanation is given.

22.4.2.4 Prep factor and dilution calculations by LIMS are present in the data report and LIMS calculations are correct.

22.4.2.5 LCS and Spike Recoveries and RPD calculations by LIMS are correct and are within control limits.

22.4.3 Valildation: Before data is reported out of the lab:

22.4.3.1 Analyst and Peer Level reviews have been completed and any corrections or comments made.

22.4.3.2 Preparation data has been entered and reviewed by a peer.

22.4.3.3 Analytical data is present for all analyses.

22.4.3.4 Weight/Volume, dilution, spike recovery, RPD, and LCS recoveries appear to be calculated correctly.

22.4.3.5 All forms, raw data and log sheets requested by the client are present.

22.4.3.6 Results are accurate on forms (see GL-MA-E-017).

22.5 Documentation and review process is reflected in the Data Review Flow Chart in Appendix 1.

23.0 DATA REPORT

23.1 To report data after the review process has been completed:

23.1.1 Enter the LIMS program through GEL home page and click on ALPHALIMS Application.

23.1.2 Click on MAINTAIN BATCHES and type in the queue at SELCT A QUEUE (ICP for Industrial and ICPF for Federal).

23.1.3 Select batch number at SAMPLE ID column, and the run status will show whether data is ready to calculate.

23.1.4 When data is ready to calculate, click on CAL.

23.1.5 Click on SAVE to save the data.

23.1.6 Send data to review at STATUS column for quality purposes.

23.1.7 Print data, initial and date for final review.

23.2 The Final Reviewer is responsible for changing the batch status to DONE in ALPHALIMS and to initial and date the data report. The Final Reviewer is also responsible to make a copy of the data report and run log. (ONLY FOR FEDERAL.)

24.0 RECORDS MANAGEMENT AND DOCUMENT CONTROL

24.1 Records of the instrumental analysis, operation, and maintenance are maintained as follows:

24.1.1 Run logs are an accurate chronology of what the instrument did during a specified period of time. It details the standard name or sample number for each standardization or analysis; the analyst identification; and the date and time of each analysis or standardization. This information is periodically retrieved from the instrument data files, printed in chronological sequence, and maintained as documentation of the sequence of events and as a reference for the raw data.

24.1.2 Extraction/Digestion Logs are maintained in accordance with the established procedures in the areas where these processes are performed.

24.1.3 Instrument Maintenance Logs are chronological representations of all maintenance activities involving the instrument operation. This record is kept in bound composition books and consists of the details of the action, who performed it, when it was performed, and when instrument was returned to operation.

24.1.4 Batch Sheets accompany the batch of samples through digestion and analysis and then accompanies the raw analytical data through data entry and data review until the batch status is changed to "DONE" in the laboratory. The person responsible for each of these actions writes their initials and date

completed on the batch sheet. This record is maintained in the Metals group files.

24.1.5 Batch Data Reports are generated from LIMS after the data is entered and is attached to the batch sheet to be used in the peer review and validation. After the batch is reviewed, corrected if necessary, and updated to "DONE", the batch data report is stored with the Batch sheet.

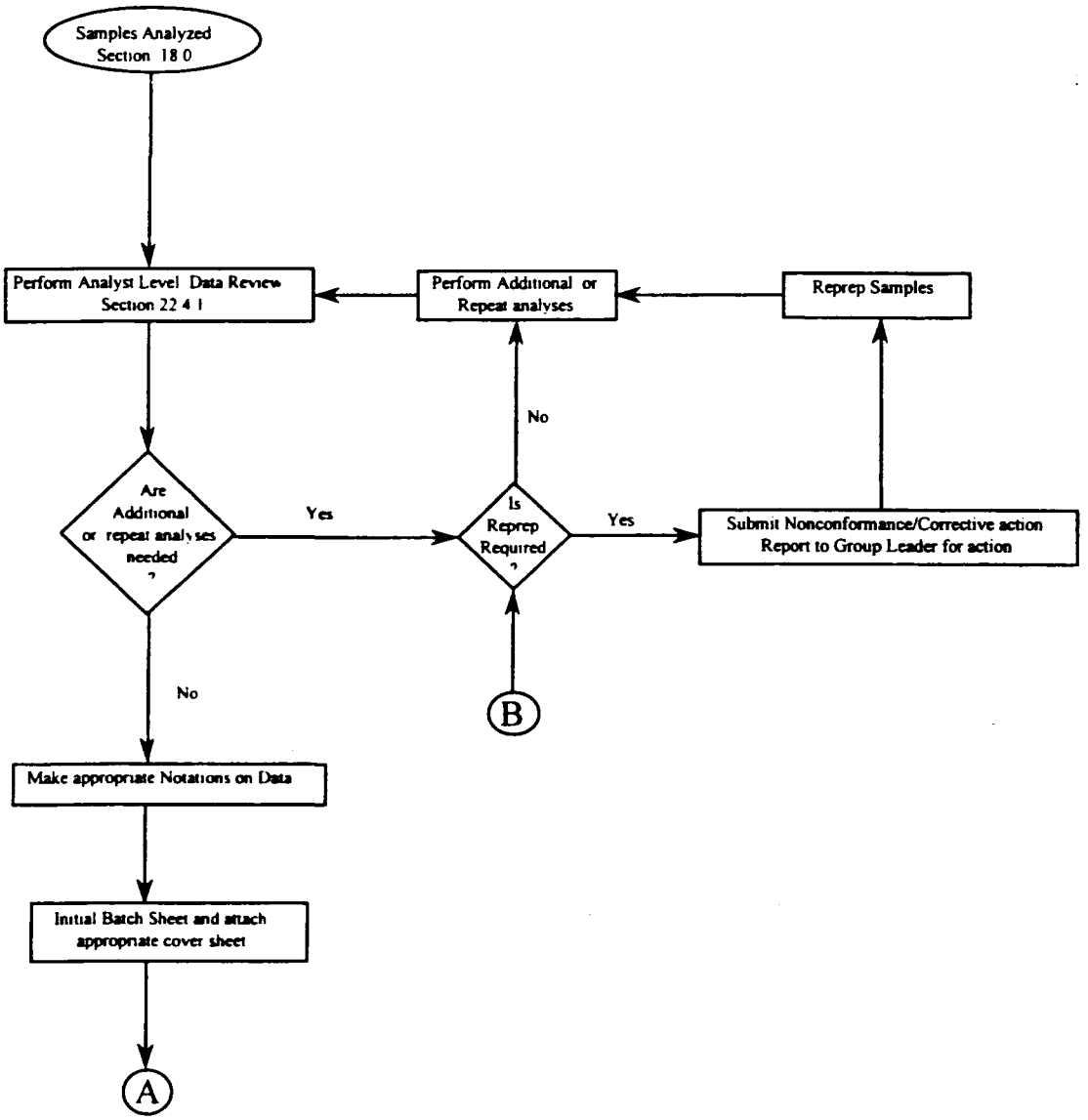
24.1.6 Raw Instrument Data is generated as the analyses are performed and is used in the data review process and kept in the Metals group files.

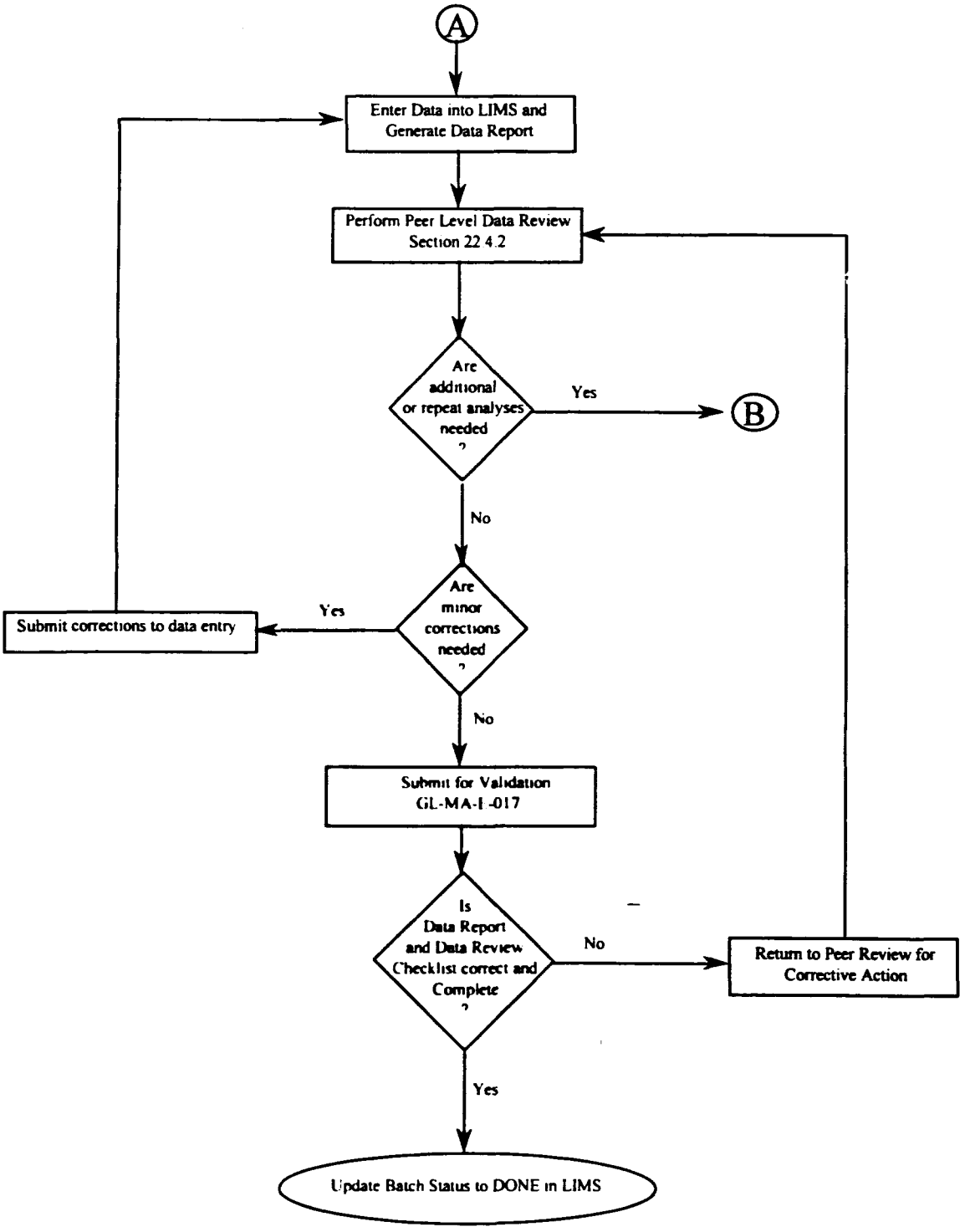
25.0 LABORATORY WASTE HANDLING AND DISPOSAL

All Laboratory wastes are handled and disposed in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

APPENDIX 1: Production Flow Chart
(For Illustrative Purposes Only)

Data Review Flow Chart




A
Enter Data into LIMS and Generate Data Report
Perform Peer Level Data Review Section 22 4.2
Are additional or repeat analyses needed ?
Yes
B
No
Are minor corrections needed ?
Yes
Submit corrections to data entry
No
Submit for Validation GL-MA-E-017
Is Data Report and Data Review Checklist correct and Complete ?
No
Return to Peer Review for Corrective Action
Yes
Update Batch Status to DONE in LIMS

APPENDIX 2: CALIBRATION STANDARDS FOR TRACE

(for illustrative purposes only)

S0 reagent blank (3%HCl / 1%HNO3)

S0.1 0.1ppm (100ppb) As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Sr, Tl, U, V, Zn Sb, Mo, Ag, Sn, Ti

0.2ppm (200ppb) S

0.5ppm (500ppb) Si, P

1ppm (1000ppb) Al, Ca, Mg, K, Na

S0.5 0.5ppm (500ppb) As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Sr, Tl, U, V, Zn Sb, Mo, Ag, Sn, Ti

1ppm (1000ppb) S

2.5ppm (2500ppb) Si, P

5ppm (5000ppb) Al, Ca, Mg, K

SCAL 1ppm (1000ppb) As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Sr, Tl, U, V, Zn Sb, Mo, Ag, Sn, Ti

2ppm (2000ppb) S

5ppm (5000ppb) Si, P

10ppm (10000ppb) Al, Ca, Mg, K, Na

S10 50ppm (50000ppb) Ca, Al, Mg
20ppm (20000ppb) Fe, Na

(Analytes and concentrations may change with further method development)

APPENDIX 3: FREQUENCY OF QUALITY CONTROL ACTIVITIES

(for illustrative purposes only)

Frequency of Quality Control Activities

Method/ Frequency	SW-846 6010B	EPA 200.7	200.7 CLP-M
Calibration Std readbacks	Not required	Not required	95% - 105% per calibration
Linear Range Std	Quarterly (may be more frequent per contract)	Quarterly (may be more frequent per contract)	Quarterly (may be more frequent per contract)
ICV	Per calibration	Per calibration	Per calibration
ICB	Per calibration	Per calibration	Per calibration
PQL/CRI (CLP)	Per calibration	Per calibration	Per calibration; end of analytical run
ICSA	Per calibration	Per calibration	Per calibration
ICSAB	Per calibration	Per calibration	Per calibration; every 8 hours after or end of analytical run
CCV	Every 10 instrument runs	Every 10 instrument runs	Every 10 instrument runs
CCB	Every 10 instrument runs	Every 10 instrument runs	Every 10 instrument runs
Method Blank	5% or per batch	5% or per batch	5% or per batch
LCS - liquid LCS - soil	5% or per batch	5% or per batch	5% or per batch
Matrix Spikes	5% or per request	10% or per request	5% or per request
Sample Duplicates	5% or per request	5% or per request	5% or per request
Serial Dilutions	5% or per request	5% or per request	5% or per request

APPENDIX 4: ACCEPTANCE LIMITS

Method/ Acceptance Criteria	SW-846 6010B	EPA 200.7	200.7 CLP-M
Calibration Std readbacks	Not required	Not required	95% - 105% per calibration
Linear Range Std	± 10% of true value	± 10% of true value	± 5% of true value
ICV	90% - 110%	95% - 105%	90% - 110%
ICB	< absolute value of RL	< absolute value of RL	< absolute value of RL
PQL/CRI (CLP)	50% - 150% advisory limits only	50% - 150% advisory limits only	50% - 150% advisory limits only
ICSA	80-120% for major components, 2XRL for others	80-120% for major components, 2XRL for others	80-120% for major components, 2XRL for others
ICSAB	80%-120%	80%-120% (may be requested)	80%-120%
CCV	90% - 110%	90% - 110%	90% - 110%
CCB	-2X RDL - RDL	-2X RDL - RDL	< absolute value of RL
Method Blank	-2X RDL - RDL	-2X RDL - RDL	< absolute value of RL
LCS - liquid LCS - soil	80% - 120% current SPC limits	85% - 115% current SPC limits	85% - 115% current SPC limits
Matrix Spikes	75% - 125%, when applicable	75% - 125%, when applicable	75% - 125%, when applicable
Sample Duplicates	0% - 20% when greater than 5X RL, +/-RL when less than 5X RL	0% - 20% when greater than 5X RL, +/-RL when less than 5X RL	0% - 20% when greater than 5X RL, +/-RL when less than 5X RL
Serial Dilutions	0% - 10% of initial raw value, when applicable	0% - 10% of initial raw value, when applicable	0% - 10% of initial raw value, when applicable

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

MERCURY ANALYSIS USING THE PERKIN ELMER

AUTOMATED MERCURY ANALYZER

(GL-MA-E-010 REVISION 13)

APPLICABLE TO METHODS:

EPA SW-846 Methods: 7470A and 7471A
EPA Methods: 245.1, 245.2 and 245.5
EPA Methods 245.1 CLP-M, 245.2 CLP-M and 245.5 CLP-M
Standard Method 3112B

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GEL's Document Control Officer certifies this document to be a true copy of the fully executed original.

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1.0 STANDARD OPERATING PROCEDURE FOR MERCURY ANALYSIS USING THE PERKIN ELMER AUTOMATED MERCURY ANALYZER

2.0 METHOD OBJECTIVE AND SUMMARY

This Standard Operating Procedure (SOP) describes the digestion and analysis procedures for the determination of mercury (Hg) in surface and saline waters, wastewaters, industrial effluents, sanitary sewage, soils, sediments, bottom deposits, sludges, oils, and TCLP extracts. This is a cold-vapor atomic absorption technique based on the absorption of radiation at 253.7 nm by mercury vapor. Samples are treated with nitric acid and sulfuric acid or hydrochloric acid in the presence of potassium permanganate and potassium persulfate to oxidize all mercury to the mercuric (Hg^{++}) form. The mercury is then reduced to its elemental state and evacuated from the sample. The mercury vapor passes through an optical cell positioned in the light source of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. This SOP is applicable for the following methods:

2.1 EPA SW-846 Methods 7470A and 7471A
2.2 EPA Methods 245.1, 245.2 and 245.5
2.3 EPA Methods 245.1 CLP-M, 245.2 CLP-M and 245.5 CLP-M
2.4 Standard Method 3112B

3.0 METHOD APPLICABILITY

3.1 Calibration Range - The typical calibration range used for analysis of mercury is 0.2 µg/L to 10.0 µg/L. Other calibration ranges (e.g. 0.1 µg/L to 5.0 µg/L) may be used per client/contract request.

3.2 Tested Concentration Range - The range for the method is limited by calibration and can be extended by diluting the sample.

3.3 Method Detection Limit (MDL) - The MDL is calculated using the procedure described in "The Determination of Method Detection Limits" (GL-LB-E-001). The MDL is verified quarterly, or whenever there is a significant change in the instrument response.

3.4 Instrumental Detection Limits (IDL) - IDLs are determined on a quarterly basis per EPA CLP, Inorganic Statement of Work, ILM04.0, Exhibit E, Section V. IDLs are performed on three non-consecutive days.

3.5 Method Precision - Analytical precision can be determined by calculating the Relative Percent Difference (RPD) between a Laboratory Control Sample (LCS) and a Laboratory Control Sample Duplicate (LCSD) or a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD).

3.6 Method Bias (Accuracy) - Accuracy can be determined by calculating recoveries of a LCS and LCSD or an MS and MSD of a similar matrix.

4.0 DEFINITIONS

4.1 Tumble Blank (TB) – TCLP extraction fluid Type 1 or 2 that has been taken through the TCLP tumbling process. The tumble blank is used to determine the amount of background contamination resulting from the tumbling process.

4.2 Method Blank (MB) - Type I water that has been taken through the digestion process. The method blank is used to determine the amount of background contamination resulting from the digestion process.

4.3 Laboratory Control Sample (LCS) - A certified reference material that has been taken through the digestion process. The LCS is used to determine digestion accuracy and to determine if the digestion is in control.

4.4 Laboratory Control Sample Duplicate (LCSD) - A duplicate of the LCS. The LCSD is used to determine reproducibility and to indicate precision.

4.5 Matrix Spike (MS) - A sample that has added to it a known amount of solution containing known concentrations of analytes. The MS is used to determine the presence or absence of interferences and matrix effects in the digested sample.

4.6 Matrix Spike Duplicate (MSD) - A duplicate of the MS. The MSD indicates reproducibility.

4.7 Sample Duplicate (DUP) - A duplicate of a sample. The DUP indicates reproducibility.

4.8 Method Detection Limit (MDL) - The minimum concentration of an analyte that can be measured and reported with 99% confidence that the concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix type containing the analyte.

4.9 Instrument Detection Limit (IDL) - Determined by multiplying by three the standard deviation obtained for the analysis of a prepared standard solution of Hg at a concentration three to five times the manufacturer's IDL on three non-consecutive days with seven consecutive measurements per day.

5.0 METHOD VARIATIONS

This SOP varies from the referenced methods by utilizing a smaller sample aliquot. Reagent amounts are adjusted accordingly.

6.0 SAFETY PRECAUTIONS AND WARNINGS

WARNING

HYDROXYLAMINE HYDROCHLORIDE MAY EXPLODE WHEN HEATED TO 140 °C.

MERCURY COMPOUNDS ARE TOXIC IF INHALED OR ABSORBED THROUGH THE SKIN.

ADDITION OF HCl AND HNO_3 IN THE PROPORTIONS 3 TO 1 FORMS AQUA REGIA.

ADDITION OF HYDROXYLAMINE HYDROCHLORIDE - SODIUM CHLORIDE TO AQUA REGIA CAN CAUSE THE SPONTANEOUS RELEASE OF CL_2 GAS. PERFORM DIGESTIONS USING AQUA REGIA UNDER A HOOD.

NITRIC ACID AND SULFURIC ACID ARE HIGHLY CORROSIVE.

CONTACT WITH OXIDIZERS MAY GENERATE EXPLOSIVE MIXTURES.

NITRIC ACID IS CORROSIVE AND A POISON.

MERCURY VAPORS ARE TOXIC. DIGEST SAMPLES AND STANDARDS UNDER A FUME HOOD.

WHEN DIGESTING SOIL, OIL, AND SEDIMENT, BE CAREFUL TO AVOID INHALING TOXIC NO_X.

WARNING

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

6.1 Wear eye protection with side shields while performing procedures in the lab.

6.2 Treat all chemicals as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). These documents and individual sample MSDS forms are maintained in the laboratory.

6.3 Personal protective equipment

6.3.1 Gloves are required when handling the chemicals in this procedure.

6.3.2 Work under a hood when using concentrated acids and bases.

6.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

6.4.1 Protect counter tops with counter paper or work from radioactive sample handling trays.

6.4.2 Prohibit admittance to immediate work area.

6.4.3 Post signs indicating radioactive samples are in the area.

6.4.4 Take swipes of the counter tops upon completion of work. Deliver those swipes to the appropriate swipe count box.

6.4.5 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

6.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

6.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

6.7 In the event of an accident or medical emergency, call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

6.8 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

7.0 INTERFERENCES TO THE METHOD

7.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

7.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

7.3 Seawaters, brines, and industrial effluents high in chlorides may require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs at 253.7 nm.

7.4 Certain volatile organic materials that absorb at 253.7 nm may also cause interference.

8.0 APPARATUS AND MATERIALS; REAGENTS; EQUIPMENT AND INSTRUMENTS

8.1 Ancillary Equipment

8.1.1 50 mL digestion tubes
8.1.2 Flask, Volumetric, (100 mL and 250 mL)
8.1.3 Variable and single volume Pipette and Micro Pipettes
8.1.4 Hot Block (Temperature controlled at 95° ± 5° C)
8.1.5 Non-Mercury thermometers
8.1.6 Culture tubes

8.2 Reagents:

8.2.1 Type I water - Water that conforms to the following performance specifications:

8.2.1.1	Electrical resistivity, min.,	16.67
8.2.1.2	Total organic carbon, max., µg/L	100

8.2.1.3	Sodium, max., µg/L	1
8.2.1.4	Chlorides, max., µg/L	1
8.2.1.5	Total silica, max., µg/L	3

Type I water is dispensed within the metals prep lab by the "MilliQ" water system.

8.2.2 Nitric Acid (HNO_3), Concentrated, ACS grade certified for AA use.

8.2.3 Sulfuric Acid (H_2SO_4), Concentrated, ACS grade certified for AA use.

8.2.4 Hydrochloric Acid (HCl), Concentrated, ACS grade certified for AA use.

8.2.5 3% HCl: Dissolve 30 mL concentrated HCl in Type I water and dilute to 1000 mL. Volume may be scaled proportionately.

8.2.6 Potassium Permanganate Solution ($KMnO_4$), 5%: Dissolve 5 g potassium permanganate in Type I water and dilute to 100 mL. Volume and weight may be scaled up proportionally.

8.2.7 Potassium Persulfate Solution ($K_2S_2O_8$), 5%: Dissolve 5 g potassium persulfate in Type I water and dilute to 100 mL. Volume and weight may be scaled up proportionally.

8.2.8 Sodium Chloride-Hydroxylamine Hydrochloride Solution (NaCl- NH_2OH HCl): Dissolve 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride in Type I water and dilute to 100 mL. (Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.) Volume and weight may be scaled up proportionally.

8.2.9 Stannous Chloride Solution ($SnCl_2$), 1.1%: Dissolve 11 g stannous chloride in 3% hydrochloric acid and dilute to1 L. Volume and weight may be scaled proportionately.

8.2.10 Aqua regia: Combine 3 parts conc. HCl and 1 part conc. HNO_3. Prepare fresh before use.

NOTE: Due to the inherent dangers of working with full strength Aqua regia, a 1+1 solution is prepared for use with the sample preparation.

8.2.11 Mercury Source Standard (Hg), 1000 ppm, from an Approved Vendor. Standards are received, labeled, prepared and stored according to GL-LB-E-007 for Laboratory Standards Documentation.

8.2.12 Liquid Nitrogen or Compressed Nitrogen at pressures 75-100 psi.

8.3 Instrumentation

8.3.1 Perkin Elmer FIMS400 and FIMS100 Automated Mercury Analyzers

8.3.2 Balance

9.0 SAMPLE HANDLING AND PRESERVATION REQUIREMENTS

9.1 Aqueous samples must be acidified to a pH <2 with HNO_3. The suggested maximum holding time for these samples is 28 days. When performing CLP analyses, the holding time is 26 days from verified time of sample receipt.

9.2 Non-aqueous samples shall be refrigerated and analyzed as soon as possible. The preservation required for soil/sediment samples is maintenance at 4° ± 2°C until analysis.

9.3 TCLP extracts have a maximum holding time of 28 days before extraction and 28 days after extraction for a total of 56 days.

10.0 SAMPLE PREPARATION TECHNIQUES

10.1 Prior to determining the concentration of mercury, all samples, calibration standards, check standards, laboratory control samples, and blanks must be digested using the following procedures:

10.1.1 For standards preparation, see the Mercury recipe section of the ALPHA LIMS Standards Logbook.

10.1.2 Label each digestion tube with a sample number or lab Quality Control (QC) number. Establish a one to one relationship between client samples, QC samples, and digestion tubes.

10.2 Aqueous Sample Preparation by Methods EPA SW-846 7470A, EPA 245.1,EPA 245.2 and Standard Method 3112B

10.2.1 Transfer 20 mL of Type I water, 20 mL of a well mixed representative sample, or an aliquot of sample diluted to 20 mL with Type I water, to a labeled digestion tube. Record the volume of sample dispensed into the digestion tube in the Mercury Prep logbook.

10.2.2 For TCLP and MISC-L matrices, transfer 18 mL of Type I water, 2 mL of a well-mixed representative sample, or an aliquot of sample diluted to 20 mL final volume, to a labeled digestion tube. Record the volume of sample dispensed into the digestion tube in the Mercury Prep logbook.

10.2.3 The following calibration standards are required: 0.2, 0.5, 2.0, 5.0, 10.0 µg/L, ICV/CCV, ICB/CCB, and CRA. Other calibration standards may be prepared per client request.

10.2.4 Add the appropriate amount of spiking solution to each appropriate QC sample tube. Add 0.5 mL concentrated HNO_3 and then 1.0 mL concentrated H_2SO_4 to each digestion tube and mix.

10.2.5 Add 3 mL of 5% $KMnO_4$ solution to each digestion tube and mix. Let sample stand for 15 minutes after addition of $KMnO_4$. If sample does not maintain its brown/purple color, add an additional 3 mL aliquot of the 5% $KMnO_4$ to the sample and all associated QC. Record this additional aliquot on the comment section of the Mercury Prep logbook. If after the second aliquot is added, the sample is still not able to maintain its purple/brown color throughout the digestion process, then redigest the sample using an appropriate dilution.

10.2.6 Add 1.5 mL of 5% $K_2S_2O_8$ solution to each digestion tube and mix. Cap each digestion tube and place in a Hot Block for two hours at 95° ± 5°C.

10.2.7 After two hours, remove digestion tubes from the Hot Block and allow to cool. Cooling can be facilitated by moving samples to the walk-in cooler for no greater than 90 minutes. When the samples have been cooled to room temperature, add 1 mL of $NaCl\text{-}NH_2OH\cdot HCl$ solution to each digestion tube to reduce any excess $KMnO_4$. Cap tubes and shake until the samples are fully reduced. The samples are now ready for analysis.

10.3 Sediment, Oil and Soil Sample preparation by Methods EPA SW-846 7471A, and EPA 245.5

10.3.1 Weigh triplicate 0.2 g portions of a representative sample (for a total of approximately 0.6 grams) and place all three aliquots into a digestion tube. Record the weight in the Mercury Prep logbook. LCS water is used for oil or any other samples that are not a soil or in soil form.

10.3.2 The following calibration standards are required: 0.2, 0.5, 2.0, 5.0, 10.0 µg/L, ICV/CCV, ICB/CCB, and CRA. Other calibration standards may be prepared per client specification.

10.3.3 Add 5 mL of Type I Water to each tube. Add the appropriate amount of spiking solution to each appropriate QC sample tube. Add 3 mL of 1+1 Aqua regia to each sample and associated QC and mix.

10.3.4 Place each digestion tube in a Hot Block at 95° ± 5°C for two minutes.

10.3.5 Remove digestion tubes from the Hot Block. Cool for at least 15 minutes. Then add 25 mL of DI water and 7.5 mL of 5% $KMnO_4$ solution and mix thoroughly.

10.3.6 Cap each digestion tube and again place each digestion tube in a Hot Block 95° ± 5°C for 30 minutes.

10.3.7 Remove tubes from the Hot Block and allow to cool to room temperature for at least 60 minutes.

10.3.8 **CAUTION**: This next step can cause Cl_2 gas to be generated. Perform the following step under a hood.

10.3.9 Uncap the digestion tubes under a hood. Add 2 mL of sodium chloride-hydroxylamine hydrochloride solution to each tube. Cap and shake until samples are fully reduced. Uncap and allow time for Cl_2 gas to evolve and vent from the digestates. The samples and standards are now ready for analysis.

10.4 Aqueous Sample Preparation by method 245.1 CLP-M and 245.2 CLP-M

NOTE: If client permits, the reduced volume sample preparation described in section 12.1.3 will be employed in order to reduce laboratory waste.

10.4.1 Transfer 20 mL of Type I water, 20 mL of a well-mixed representative sample, or an aliquot of sample (containing not more than 1.0 µg of mercury) diluted to 20 mL with Type I water, to a labeled digestion tube. Record the volume of sample dispensed into the digestion tube in the Mercury Prep logbook.

10.4.2 For TCLP and MISC-L matrices, transfer 18 mL of Type I water, 2 mL of a well-mixed representative sample, or an aliquot of sample diluted to 20 mL final volume, to a labeled digestion tube. Record the volume of sample dispensed into the digestion tube in the Mercury Prep logbook.

10.4.3 The following calibration standards are required: 0.2, 0.5, 2.0, 5.0, 10.0 µg/L, ICV/CCV, ICB/CCB, and CRA. Other calibration standards may be prepared per client specification.

10.4.4 Add the appropriate amount of spiking solution to each appropriate QC sample tube. Add 0.5 mL concentrated HNO_3 and then 1.0 mL concentrated H_2SO_4 to each digestion tube and mix.

10.4.5 Add 3 mL of 5% $KMnO_4$ solution to each digestion tube and mix. Let sample stand for 15 minutes after addition of $KMnO_4$. If sample does not maintain its brown/purple color, add an additional 3 mL aliquot of the 5% $KMnO_4$ to the sample and all associated QC. Record this additional aliquot on the comment section of the Mercury Prep logbook. If after the second aliquot is added, the sample is still not able to maintain its purple/brown color throughout the digestion process, then redigest the sample using an appropriate dilution.

10.4.6 Add 1.5 mL of 5% $K_2S_2O_8$ solution to each digestion tube and mix. Cap each digestion tube and place in a Hot Block for two hours at 95° ± 5°C.

10.4.7 After two hours, remove digestion tubes from the Hot Block and allow to cool. Cooling can be facilitated by moving samples to the walk-in cooler for no greater than 90 minutes. When the samples have been cooled to room temperature, add 2 mL of $NaCl\text{-}NH_2OH\cdot HCl$ solution to each digestion tube to reduce any excess $KMnO_4$. Cap tubes and shake until samples are fully reduced. The samples are now ready for analysis.

10.5 Soil/Sediment Sample Prep by method EPA 245.5 CLP-M

10.5.1 Weigh triplicate 0.2 g portions of a representative samples (for a total of approximately 0.6 grams) and place all three aliquots into a digestion tube. Record each weight on the Mercury Prep logbook.

10.5.2 The following calibration standards are required: 0.2, 0.5, 2.0, 5.0, 10.0 µg/L, ICV/CCV, ICB/CCB, and CRA. Other calibration standards may be prepared per client specification.

10.5.3 Add 5 mL of Type I Water to each tube. Add the appropriate amount of spiking solution to each appropriate QC sample tube. Add 3 mL of 1+1 Aqua regia to each sample and associated QC and mix.

10.5.4 Place each digestion tube in a Hot Block at 95 ± 5° C for two minutes.

10.5.5 Remove digestion tubes from the Hot Block. Cool for at least 15 minutes. Then add 25 mL of DI water and 7.5 mL of 5% $KMnO_4$ solution and mix thoroughly.

10.5.6 Cap each digestion tube and again place each digestion tube in a Hot Block at 95 ± 5°C for 30 minutes.

10.5.7 Remove tubes from the Hot Block and cool to room temperature for at least 60 minutes.

10.5.8 **CAUTION:** This next step can cause Cl_2 gas to be generated. Perform the following step under a hood.

10.5.9 Uncap the digestion tubes under a hood. Add 3 mL of sodium chloride-hydroxylamine hydrochloride solution to each tube. Cap and shake each tube until samples are fully reduced. Uncap and allow time for Cl_2 gas to evolve and vent from the digestates. The samples and standards are now ready for analysis.

11.0 PREPARATION OF STANDARD SOLUTIONS AND QUALITY CONTROL SAMPLES

11.1 Source standard solutions

11.1.1 Source standard solutions are purchased from a certified vendor. These standards are traceable to National Institute of Standards and Technology (NIST) standards. The source standards are received from Purchasing.

11.2 Intermediate and working standards must be PREPARED FRESH DAILY.

11.3 For guidance on standard documentation, refer to "Laboratory Standard Documentation" (GL-LB-E-007).

11.4 For Kerr-McGee Samples, reprep and reanalyze the samples if MB or CCB is greater than the RL and samples are between IDL and RL. If samples are less than IDL or greater than 10 times the RL they can be reported.

12.0 INSTRUMENT CALIBRATION AND PERFORMANCE

12.1 Instrument calibration is performed using the following prepared mercury standards: 0.0, 0.2, 0.5, 2.0, 5.0 and 10.0 µg/L.

12.2 An example of a data calculation based on fictitious information follows. Other concentrations may be employed for the calibration curve and ICV.

CONCENTRATION	%RSD	INSTRUMENT RESPONSE
0.0 µg/L	8.2760	0.0007
0.2 µg/L	0.7089	0.0023
0.5 µg/L	1.3778	0.0059
2.0 µg/L	1.6793	0.0243
5.0 µg/L	0.5449	0.0600
10.0 µg/L	1.6070	0.1160

12.3 Performing a linear regression on these data, using the instrument response as the independent variable and the concentration as the dependent variable results in a slope = 86.103, intercept = -0.0521, and a correlation "r" = 0.9998. Thus the concentration of a sample will be calculated by solving the equation:

Concentration (µg/L) = 86.103 (instrument response) – 0.05214

TRUE VALUE	SAMPLE NAME	INSTRUMENT RESPONSE	CALCULATED LINEAR (µg /L)
0.5 µg	ICV	0.00580	0.4447
0.0 µg	ICB	0.0002	0.02
0.2 µg	0.2 CRA	0.0026	0.17

12.4 Report data to the appropriate number of significant figures.

12.5 Data is reported in µg/L, mg/L, µg/Kg or mg/Kg Hg depending on client preference. Sample units are defined before data is input into the laboratory information management system by the analyst.

12.6 Any sample concentration less than 100% of the highest recorded calibration standard is acceptable. If sample concentrations are over 100% of the high standard, then these samples must be re-analyzed at a dilution that will bring the sample concentration within the range. Dilutions are made with digested blanks.

12.7 A CRDL standard for AA (CRA) is required to be run following calibration. The result of the CRA should be within the range per client request. When performing CLP analyses, the acceptance criteria for the CRDL standard (CRA) has not yet been established by EPA.

12.8 The acceptable performance requirements for the Hg instrument are a verification of stability by showing that there is no drift, correlation coefficient of 0.995 or better, and ICV and CCV within the acceptance range prescribed in Section 16.2.

12.9 Proof of instrument performance during actual sample analysis is provided by records of the calibration curve, ICV, CCV, and CCB.

13.0 ANALYSIS AND INSTRUMENT OPERATION

13.1 Before actual operation, all samples, including standards and QC samples, are prepared and digested as described in Section 10. Instrument operation includes a calibration phase and a sample analysis phase. The two phases are usually run as one continuous procedure, but the instrument may be calibrated prior to loading and running samples. Also note that the analyst needs to monitor the process to ensure that the calibration is satisfactory prior to analyzing samples. If the calibration process is unsatisfactory it will need to be terminated, problems corrected, and the calibration rerun.

13.2 Turn on computer.

13.3 Use password "hg1" for FIMS400 and "hg2" for FIMS100.

13.4 Turn on Hg FIMS instrument – note that the autosampler initializes. Let it warm up for at least 30 minutes.

13.5 Prepare daily-1.1% $SnCl_2$ reducing solution in 3% HCl in amber bottle. Shake well and put in the appropriately labeled reductant reservoir bottle that feeds the instrument.

13.6 Fill other instrument reservoir bottle with 3% HCl for instrument rinse and carrier acid.

13.7 Double-click AA WinLab Analysis icon.

13.8 Click on the middle button [automated analysis].

13.9 Click [Sample Info] button.

13.10 The standards will be in positions 1-11 and they are already entered into the system, but don't show up here (1-BC, 2-0.2 ppb, 3-0.5 ppb, 4-2.0 ppb, 5-5.0 ppb, 6-10 ppb, 7-CCV, 8-CCB, 9-ICV, 10-ICB, 11-CRDL. Go to Autosampler location 12 to type in information from batch sheet.

13.11 #12 – enter sample Ids from Batch Sheet following the naming convention outlined in the instrument user manual.

13.12 File: save as sample file info (name it with the "yymmdd", followed by W# for waters or S# for soils). (The # indicates the FIMS model used.)

13.13 Click (Auto) button.

13.14 Double click on #1 cell, select the soil or water method as appropriate from the list [OK]. They are Water1 or Soil1 depending on matrices.

13.15 Sample info file: browse, select your "mmddyy" [OK].

13.16 Result data set name: browse, enter "mmddyy" [OK].

13.17 Double click on the line under "method" and click on the box under "use entire sample info file". An "x" will appear in the box.

13.18 Check the [Cont] icon button by clicking on the icon. Remove the FIMS cell, and then click on Autozero. Re-install the FIMS cell.

13.19 Load standards. Put standards in the autosampler rack.

13.20 Load samples beginning in position #12. Note that samples go in the 15 ml digestion tubes. A CCV and CCB must separate each group of 10 samples. All samples must be bracketed by a satisfactory CCV and CCB.

13.21 Install new membrane filter, rough side up (in final assembly position). Screw cap on tightly.

13.22 Hook up and clamp pump tubing. Check all pump tubing daily.

13.23 Click [FIAS] button icon.

13.24 To flush things out: Click [pump 1] (adjust to 100 rpm) and [pump 2] (adjust to 120 rpm for FIMS 400 only) icons.

13.25 Adjust gas flow to 40-70 cm^3/min.

13.26 Verify flow rates of reductant (5-7 mL/min, red/red tubing) and carrier (9-11 mL/min, blue/yellow tubing) with DI water using graduated cylinders.

13.27 Cycle [valve fill/inject] to further flush things out. Give it a minute or so in each position. Unclick all three buttons and close the window.

13.28 In the "Automated Analysis" window click on "Analyze Tab" then click on [Analyze All].

14.0 EQUIPMENT AND INSTRUMENTATION MAINTENANCE

14.1 If there are problems: During the analysis the foreground window is usually the "Results" text window that is also automatically printed, and the background window is the "Automated Analysis" window. If you need to abort a run, you must wait for the hourglass mouse cursor to change to an arrow, then click on the "Automated Analysis" window to bring it to the foreground. Then unclick the [Analyze All] button. A dialog box will come up giving you a couple of options.

14.2 For non-routine maintenance procedures see Perkin Elmer manual for troubleshooting.

14.2 Whenever instrument is serviced or adjusted, an entry needs to be made in the maintenance log. The entry includes the analyst's initials, date, nature of the problem, and actions taken to correct it.

15.0 DATA RECORDING, CALCULATIONS AND DATA REDUCTION

15.1 The concentration of Hg can be determined by comparing the response obtained from analyzing the sample digestate to the calibration curve. The sample concentration of Hg is matrix specific and is calculated as follows:

15.1.1 Aqueous Sample

$$\text{Concentration } (\mu g/l) = \frac{(C)(D)(V_t)}{V_i}$$

Where:

C = Concentration (µg/l) digestate
D = Dilution Factor
V_t = Total Volume of sample digestate
V_i = Initial Volume of sample in L

15.1.2 Non-aqueous Samples

$$\text{Concentration } (\mu g/kg) = \frac{(C)(D)(V_t)}{W(\%S)}$$

Where:

C = Concentration (µg/ml) digestate

D = Dilution Factor
V_t = Total Volume of the sample digestate
W = Weight of the sample digested
%S = Percent Solids

16.0 QUALITY CONTROL REQUIREMENTS

16.1 Frequency of Quality Control Activities

16.1.1 ICV is performed immediately following each calibration and CCV is performed after every 10 analysis.

16.1.2 ICB is performed immediately following the ICV and CCB must follow each CCV.

16.1.3 A method blank is analyzed for each batch of 20 or less samples.

16.1.4 A matrix spike and matrix spike duplicate or matrix spike and a sample duplicate are analyzed for every 20 or less samples in a batch, or per client requirements. When performing CLP analyses, the requirement for matrix spike analysis is one per every sample delivery group (SDG) of 20 samples or less.

16.1.5 A LCS is analyzed with each batch of 20 or less samples. Additionally, a LCS duplicate also may be analyzed due to client specific requirements.

16.2 Acceptance Limits

16.2.1 Acceptance limits for the following methods are outlined below:

Method/ Acceptance Criteria	SW-846 7470A SW-846 7471A SM 3112B	EPA 245.1 EPA 245.5 EPA 245.2	245.1 CLP-M 245.5 CLP-M 245.2 CLP-M
ICV	90% - 110%	95% - 105%	90% - 110%
ICB	-0.2 ug/L - 0.2 ug/L	-0.2 ug/L - 0.2 ug/L	-0.2 ug/L - 0.2 ug/L
CRA	50% - 150% advisory limits only	50% - 150% advisory limits only	50% - 150% advisory limits only
CCV	80% - 120%	90% - 110%	80% - 120%
CCB	-0.2 ug/L - 0.2 ug/L	-0.2 ug/L - 0.2 ug/L	-0.2 ug/L - 0.2 ug/L
Method Blank	-0.2 ug/L - 0.2 ug/L	-0.2 ug/L - 0.2 ug/L	-0.2 ug/L - 0.2 ug/L
LCS - liquid LCS - soil	80% - 120% Certified SPC limits from ERA	85% - 115%	80% - 120% Certified SPC limits from ERA
Matrix Spikes	75% - 125%	75% - 125%	75% - 125%
Sample Duplicates	0 - 20%	0 - 20%	0 - 20%

16.2.2 All reported sample concentrations must be less than the highest calibration standard. Samples greater than the highest calibration standard must be diluted to bring the concentration within range.

16.2.3 The ICV is prepared from a second standard source other than the source employed for initial calibration. Generally, the concentration of the ICV is 5.0 ug/L.

16.2.4 The method blank must have an absolute value below the CRDL for CLP analyses.

16.2.5 Matrix spikes, matrix spike duplicates and sample duplicates are indicators of method performance for a specific sample matrix.

Acceptance limits are based on guidelines outlined in the specific methods and are listed in the table above.

16.2.5.1 The spike percent recovery (%R) must be within the acceptance limits. Results that fall outside these limits are flagged with an "N" or "*". However, spike recovery limits do not apply when sample concentration exceeds the spike concentration by a factor of 4 or greater. This data is reported unflagged even if the %R does not meet the acceptance criteria.

16.2.5.2 The control limit of ± 20% for the relative percent difference (RPD) is used for original and duplicate sample values greater than or equal to 5X the reporting limit. A control limit of ± RL is used if either the sample or duplicate value is less than 5X the RL. In the case where only one result is above 5X the RL and the other is below, the ± RL criteria applies.

16.2.5.3 All LCS recoveries must fall within the stated acceptance limits. Statistical process control limits are established for LCS soils.

16.3 Out of Control situations

16.3.1 ICV and/or CCV failure requires recalibration of the instrument and/or preparation of new standard solutions. Samples analyzed between calibration verification that fail must be reanalyzed. An ICV or CCV that has failed may be rerun provided there is an attributable cause known to have affected the check standard only and not the previous samples. Examples of an acceptable cause may be a sample tip out of solution during analysis, no solution in the sample cup or obvious carryover in the CCV from a very high sample immediately prior to the CCV. If the CCV is reanalyzed, the data must be lined through, initialed and dated, and the reason for the rerun must be documented on the raw data. In addition, corrective action should be taken to eliminate the cause of the initial CCV failure to prevent future occurrence.

16.3.2 ICB or CCB failure requires recalibration of the instrument and/or repreparation of the calibration blank. When analyzing under SW-846, a CCB may be accepted above the RDL level under two conditions: 1) the CCB is acceptable up to the MDL level if the MDL is higher than the RDL and 2) the CCB is acceptable if the level of analyte in the CCB is less than 1/10 the analyte value in the lowest reported sample.

16.3.3 Method blank results higher than the RDL and greater than 10% of any sample value in that batch which has concentrations above the RDL requires that batch be redigested, reanalyzed, and/or reported with the appropriate qualifier. If the method blank results are less than –1X RDL, then there may be significant interference, calibration or contamination problems with the sample, instrument or calibration standards which must be resolved before the batch can be reported. When performing CLP analyses, method blank results that have absolute values higher than the CRDL and greater than 10% of any sample in the batch require that the samples be redigested and reanalyzed.

16.3.4 Matrix spikes, duplicates, and spike duplicates are used only as indicators of method effectiveness on that sample and will not be used as

acceptability criteria for the process, but the results for matrix spikes and spike duplicates must be at least higher than the sample concentration.

17.0 DATA REVIEW, APPROVAL AND TRANSMITTAL

17.1 The printout from the instrument is attached to the Laboratory Information Management System (LIMS) data report, original batch sheet, and the Mercury Prep Logbook.

17.2 The metals department analyst reviews mercury data by verifying that the values from the printout agree with values entered into the mercury data run logbook, and with the values that appear on computer printed data report sheets. The calibration standards, the correlation coefficient, CCV, LCS, duplicates, and spikes are also reviewed to make sure values are within the limits.

17.3 Levels of review responsibility are described below:

17.3.1 Analyst Review - Hg data is reviewed by the analyst after the run is complete and checked once more after data is entered in LIMS system.

17.3.2 Peer Analyst Review - Another analyst familiar with Hg and its data reviews all data in detail.

17.4 Review of each level

17.4.1 Analyst Review - Analyst checks his/her own data and makes necessary corrections on any errors (i.e. writing wrong numbers, checks correlation coefficient again, dilution factors, and continuous calibration standards).

17.4.2 Peer Analyst Review - Reviews all data on the printout, data reported in the Mercury Data Run Logbook, Mercury Prep Logbook and information that is on the computer printed data report. It is important at this level to check what preparation date was entered, dilution factors, concentrations of spikes, and CCVs. The Case Narrative Report is used to standardize items checked by peer analysts.

17.5 The complete data review process requires the use of the Mercury Prep Logbook, Prep data report, batch sheet, LIMS data report, raw instrument data, auto-run sequence record if the samples were analyzed using an autosampler, and Case Narrative Report

18.0 RECORDS

18.1 Prep data is recorded in accordance with Section 10 of this SOP.

18.2 Data from an analysis is recorded on a printout from the instrument and stored in digital format on the instrument computer or on the network server.

18.3 Reported values come from one sample run if the instrument calibration and other required instrument specifications are met. The data is reported as a raw value along with any dilution factors used.

18.4 Uploading data into LIMS

This can be done by double clicking on the icon AA Winlab Reformat (2). Open design – double click on LIMS upload, click the file name, click on save data, close the ICM window.

18.4.1 If there is no typo, double click on Convert into CSV file. Close window.

18.4.2 If there is a typo, double click on the Review Data icon. Make the necessary changes, go to file, and then exit D.

18.4.3 Double click the Upload LIMS icon and send file to the packager. Once the two window displays are gone, close the window.

18.4.4 Double click the Runlog icon. The Runlog is printed at this time and may be retrieved at the printer.

18.4.5 If there is another analyst in addition to the primary analyst, perform 19.4.1 through 19.4.3, double click the Edit Upload for Other Analysts icon and change the analyst's initials to the person performing the analysis. Save the file.

18.4.6 Double click the Run Upload for Other Analysts, and then double click on Runlog to retrieve your Runlog from the printer.

18.4.7 When this is complete, the data will be ready for review in LIMS and a data report will be generated for data validation

19.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

20.0 LABORATORY AND WASTE HANDLING AND DISPOSAL

20.1 Standard solutions that must be disposed of are transferred by the Waste Management Technician to be disposed of in accordance with the Laboratory Waste Management Plan, GL-LB-G-001.

20.2 Special caution must be taken when samples are radioactive. Handling, delivery, transfer, and disposal of radioactive samples and residues must follow the related SOPs. Persons handling radioactive materials must first pass the training course.

21.0 REFERENCES

21.1 Methods for the Determination of Metals in Environmental Samples, Supplement 1, EPA 600/R-94-111. Method 245.1, Revision 3.0, May 1994.

21.2 Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010. Method 245.5, Revision 2.3, April 1991.

21.3 Standard Methods for the Examination of Water and Wastewater, 19th Edition, pp. 3-18 - 3-19, Method 3112B (1995).

21.4 USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration, Document Number ILM04.0 and ILM04.1.

21.5 Perkin Elmer FIMS400/FIMS100 Flow Injection Mercury System.

21.6 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1A, EPA SW-846, Final Update III, June 1997. USEPA Office of Solid Waste and Emergency Response, Washington, D.C. 20460:

21.7 Method 7470A, "Mercury in Liquid Waste (Manual Cold-Vapor Technique)," Revision 1, September 1994.

21.8 Method 7471A, "Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)," Revision 1, September 1994.

21.9 Methods for Chemical Analysis of Water and Wastes, 1983, (EPA-600/4-79/020-PB84-128677).

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

TURBIDITY

APPLICABLE TO METHODS:
EPA 180.1
Standard Methods, 18th Edition, Method 2130

(GL-GC-E-037 REVISION 7)

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1.0 STANDARD OPERATING PROCEDURE FOR TURBIDITY

2.0 METHOD CODE

EPA 180.1

3.0 METHOD OBJECTIVE/PURPOSE

To determine the turbidity of water or wastewater samples in the range of 0 to 40 nephelometric turbidity units (NTU).

4.0 METHOD SUMMARY

This method is applicable to all water and wastewater that is free of debris and coarse sediment in the turbidity range of 0 to 40 nephelometric turbidity units (NTU). The intensity of the light scattered by a sample is compared to the intensity of light scattered by a standard reference solution.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

Analysis should begin as soon as possible. Analysis must begin within 48 hours from the time and date of collection until the start of analysis unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 The sample may be stored in a plastic or glass container. Minimum 100 mL should be provided.

7.2 Samples must be unpreserved.

7.3 Sample must be stored at 4° ± 2° C to minimize microbiological decomposition of solids.

8.0 INTERFERENCES/LIMITATIONS

8.1 Interferences:

8.1.1 Debris and coarse sediment will produce erratic readings.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 0.1 to 40 NTU

9.2 Calibration range: 0.02 to 1000 NTU

9.3 Method detection limit (MDL): Refer to current MDL study.

9.4 Method precision: Refer to current SPC limits.

9.5 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 NTU - Nephelometric turbidity units

10.2 Calibration blank - A portion of reagent water is run through the analysis process. This produces your null reading for your instrument.

10.3 Method blank - Reagent grade water is used to determine the level of laboratory contamination in reagents, solvents, glassware, etc.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until they have been fully trained and have demonstrated the ability to generate acceptable data. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

12.1 Sample preparation data is recorded in AlphaLIMS.

12.2 As data is obtained, it is recorded in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while in the laboratory.

13.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). Individual sample MSDS forms provided by the clients are also maintained.

13.3 4000 NTU Formazin Stock Suspension may cause skin irritation.

14.0 SAMPLE RECEIPT FOR ANALYSIS

The analyst/technician gives a list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from the cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Volumetric flasks, 100 mL

15.2 Microliter pipet with tips

15.3 Sample vials, optical quality

15.4 Turbidimeter, HF Scientific

15.5 Calculator

15.6 KimWipes

16.0 REAGENTS

16.1 DI H_2O

16.2 4000 NTU Formazin Stock Suspension (ordered from HACH)

16.3 0.02, 10, and 1000 NTU premade standards (ordered from HACH)

17.0 PREPARATION OF SAMPLES

Not Applicable

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards and their preparation is maintained in AlphaLIMS in accordance with SOP GL-LB-E-007 for Laboratory Standards Documentation.

18.2 Prepare Formazin standards by pipetting known amounts of standards into a 100 mL volumetric flask. Bring to volume with deionized water. Standards are prepared monthly for calibration and expire after 24 hours. The 0.5 NTU standarad is prepared and analyzed with every batch and is not part of the calibration.

NOTE: Shake Formazin Stock Suspension each time before pipeting to ensure even dispersion of the suspension.

STANDARD CONCENTRATION (NTU)	PARENT STANDARD VOL (ML)	PARENT STANDARD CONC (NTU)	FINAL STANDARD VOL (ML)
1000	25.0	4000	100
10	1.0	1000	100
0.02	0.2	10	100
0.5	20	10	100

18.3 Check standards: After calibrating monthly with the formazin standards, the reference standards are read from the fresh curve and assigned a value. This value is used for 1 month or until the instrument is recalibrated with fresh formazin standards.

18.4 The LCS is the 10 NTU check standard.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

Turn on the Turbidimeter and allow at least a 2-hour warm-up for maximum stability. Place 0.02 NTU reference standard into optical well.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 The instrument manufacturer has a preset correlation coefficient. If it is not met an error message will appear and recalibration is required.

20.2 Frequency of QC:

20.2.1 A matrix duplicate is run for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples.

20.2.2 MB, LCS, 0.02 NTU and 1000 NTU reference standards are run once for each set of 20 samples in a batch or once for batches that contain ≤ 20 samples.

20.2.3 A 0.5 NTU standard is analyzed with every batch to ensure accuracy at the regulatory level.

20.3 Acceptance limits:

20.3.1 Matrix relative percent difference (RPD): See current control chart

20.3.2 Method blank: < 0.1 NTU

20.3.3 LCS: See current control chart

20.3.4 Check standards: +/-10% maximum.

20.4 Handling out-of-control situations:

20.4.1 Samples > 40 NTU must be diluted with DI water and reanalyzed.

20.4.2 If an error message appears after calibration, recalibrate or see the manufacturer's guide for troubleshooting.

20.4.3 If method blank is above lowest standard, rerun blank sample.

20.4.4 If the check standard fails, repeat the check standard. If second check standard fails, repeat analysis.

21.0 RUN SEQUENCE

21.1 Calibration standards: 0.02, 10.0, 1000 NTU

21.2 LCS (10 NTU reference standard)

21.3 Method blank

21.4 Samples 1 through x where x ≤ 10

21.5 Sample x duplicate

21.6 Check standard 10.0 NTU

21.7 Repeat steps 21.3 - 21.6 for each sequence of 10 samples

21.8 0.5 NTU check standard.

22.0 PROCEDURE

22.1 Calibration standards

NOTE: Cuvettes must be clean and free of smudges or scratches. Clean by washing in a detergent solution then rinsing thoroughly 8 to 10 rinses in distilled water to remove all streaks.

22.1.1 Being careful to avoid entrapment of air bubbles, transfer well shaken standard to sample cuvette. Wipe with lint free wipes ensuring no smudges or fingerprints are on the sample cuvette. Place vial in unit sample well.

NOTE: Settling particles or air in the sample may cause the digital reading to change rapidly. Readings are taken as soon as instrument stabilizes but before turbid particles settle.

22.1.2 Record the concentration, identification number, sample volume, and instrument reading obtained for each standard in the appropriate columns in AlphaLIMS.

22.1.3 Repeat steps 22.1.1 - 22.1.2 for each calibration standard described in section 21.1.

22.1.4 Follow the manufacturer's instructions for calibration.

22.1.5 If an error message appears after calibration, troubleshoot the cause and recalibrate. Refer to manufacturer's instructions if necessary.

22.2 Sample analysis:

NOTE: Cuvettes must be clean and free of smudges or scratches. Cleaning is accomplished by washing in a detergent solution then rinsing thoroughly 8 to 10 rinses with distilled water to remove all streaks.

22.2.1 Being careful to avoid entrapment of air bubbles, transfer well shaken sample to sample cuvette. Wipe with lint free wipes ensuring no smudges or fingerprints are on the sample cuvette. Place vial in unit sample well.

NOTE: Settling particles or air in the sample may cause the digital reading to change rapidly. Readings are taken as soon as instrument stabilizes but before turbid particles settle.

22.2.2 If turbidity exceeds 40 NTU, volumetrically dilute sample with deionized water and repeat analysis on diluted sample. Record all dilutions in the AlphaLIMS.

22.2.3 Data is entered into AlphaLIMS as it is obtained.

22.2.4 Repeat steps 22.3.1 - 22.3.3 for each sample in the batch.

22.3 Calculation/reporting of results:

22.3.1 Results are reported in NTU.

22.3.2 The RPD is calculated by subtracting the lower concentration from the higher concentration of the duplicates, dividing by the average of the two, and then multiplying the result by 100. The formula is as follows:

$$\frac{[\text{High}] - [\text{Low}]}{\text{Average of the high and low concentrations}} (100) = \text{RPD}$$

22.3.3 If the RPD is within current statistical limits or if the concentrations of both the sample and its duplicate are < the Minimum Detectable Limits, the duplicate is acceptable. If the values are above the MDL, and the RPD is greater than the current statistical limit set by the laboratory, then the sample and its duplicate are rerun.

22.3.4 For LCS recovery use the calculation below:

$$\frac{\text{obtained value}}{\text{theoretical value}} \times 100 = \text{SR\%}$$

22.3.5 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 – 1000	50
>1000	100

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Turn instrument off. Leave 0.02 NTU reference standard in optical well.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for data packaging and validation.

25.0 DATA TRANSMITTAL

When a batch is given the departmental "DONE" status, the data becomes available to reporting personnel.

26.0 RECORDS MANAGEMENT

All data associated with the activity described in this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to HF Scientific Instruction Manual.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

Method detection limit studies are conducted in accordance with GL-LB-E-001 for the Determination of Method Detection Limits.

30.0 REFERENCES

30.1 Standard Methods for the Examination of Water and Wastewater, 18th ed. pp. 2-8 through 2-11, Method 2130 (1992).

30.2 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Method 180.1 (1979).

30.3 HF Scientific Inc. MICRO 100Laboratory Turbidimeter Operators Manual

APPENDIX I

1. Press the key. Once this key is pushed the "Ident" block and the "Cal" block will illuminate on the display.
2. The turbidity value displayed in the lower row of the display should read 1000 NTU. This is the first standard that must be used in calibration. Insert the 1000 NTU calibration standard into the sample well (see figure 3) by aligning the notch and the indexing pin (see section 5.1 if you have not already indexed the standard) and wait for the reading to stabilize.
3. Press the enter key when the standard is in position. After the enter key has been pressed, the instrument will calibrate on the 1000 NTU level (the "Store" block will flash) and the upper row of the display should display 1000 NTU. The lower row of the display now shows that the 10.0 NTU calibration standard should be placed in the sample well for continuing the calibration sequence.
4. Insert the indexed 10.0 NTU calibration standard into the sample well by aligning the notch and the indexing pin (see section 5.1 if you have not already indexed the standard) and wait for the reading to stabilize.

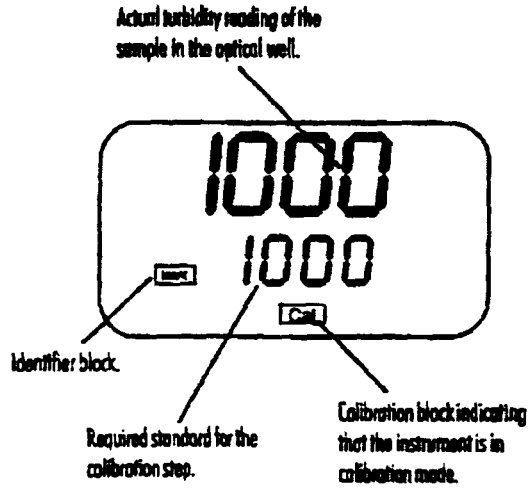

Figure 3
Display appearance during calibration of the 1000 NTU standard

5. Press the enter key when the standard is in position. After the enter key has been pressed, the instrument will calibrate on the 10.0 NTU level (the "Store" block will flash) and the upper row of the display should display 10.0 NTU. The lower row of the display now shows that the 0.02 NTU calibration standard should be placed in the sample well for continuing the calibration sequence and wait for the reading to stabilize.
6. Insert the indexed 0.02 NTU calibration standard into the sample well by aligning the notch and the indexing pin (see section 5.1 if you have not already indexed the standard).
7. Press the enter key when the standard is in position. After the enter key has been pressed, the instrument will calibrate on the 0.02 NTU level. The instrument automatically exits out of the calibration mode and then returns to the normal automatic mode. The display should read 0.02 NTU since this is the turbidity level of the standard that is still in the sample well. At this point, you have calibrated the instrument so that it measures accurately across the full range of the instrument.
8. Proceed to use the instrument normally.

NOTE: During calibration, the MICRO 100 will perform some system self-diagnostics. Several error messages may be displayed. If there is an error, one of the four error messages E01, E02, E03, and E04 will be displayed in the lower row of the display (see section 7.2).

NOTE: At any point in time during calibration, you can cycle through the required calibration points (0.02 NTU, 10 NTU, and 1000 NTU) by pressing either the or keys to individually calibrate with a particular calibration standard. If you wish to exit the calibration mode you may do so at any time by simply pressing the key. However, exiting the calibration process without completing the steps for calibration may cause the accuracy of the instrument to be diminished.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

ALKALINITY - TOTAL, BICARBONATE, CARBONATE, HYDROXIDE, AND PHENOLPHTHALEIN

(GL-GC-E-033 REVISION 2)

APPLICABLE TO METHODS:
EPA Method 310.1,
Standard Methods 18th Edition, Method 2320B

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1.0 ALKALINITY - TOTAL, BICARBONATE, CARBONATE, HYDROXIDE, AND PHENOLPHTHALEIN

2.0 METHOD CODE

2.1 EPA Method 310.1

2.2 Standard Methods 18th edition, Method 2320B

3.0 METHOD OBJECTIVE/PURPOSE

This standard operating procedure (SOP) describes the method used to determine the concentration of alkalinity (total, bicarbonate, carbonate, and hydroxide alkalinity) present in water samples.

4.0 METHOD SUMMARY

4.1 Summary: A sample aliquot is titrated with standardized sulfuric acid (H_2SO_4) solution to the phenolphthalein alkalinity (pH of 8.3) endpoint and then to the total alkalinity (pH of 4.5) endpoint. The total alkalinity concentration corresponds directly to the amount of titrant used to reach the pH 4.5 endpoint. Bicarbonate, carbonate, and hydroxide alkalinity can be determined for a sample using an alkalinity relationship table.

4.2 Synonym: Alkalinity as $CaCO_3$

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

The holding time is 14 days from the date and time of collection until the start of analysis unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples are collected in glass or plastic containers.

7.2 Samples are unpreserved. Since the alkalinity concentration determination is based on the pH of a sample, preserved samples are not analyzed.

7.3 During collection, samples should not be agitated and/or exposed to the air for a prolonged period. Both conditions could affect the pH of the sample.

7.4 Samples are stored at 4 ± 2° C in accordance with GL-SR-E-001 for Sample Receipt, Login, and Storage.

8.0 INTERFERENCES/LIMITATIONS

8.1 Interferences:

8.1.1 Oil and grease can coat the pH electrode and cause a sluggish response.

8.1.2 Salts present in large amounts can cause interference in the pH measurements.

8.1.3 Samples containing high concentrations of mineral acids should be titrated to an electromagnetic endpoint of 3.9. Refer to ASTM Standards, part 3, "WATER," D-1067, Method D (1976).

8.2 Limitations

8.2.1 Avoid titration volumes greater than 50 mL by using one of the following:

8.2.1.1 Use a more concentrated sulfuric acid titrant.

8.2.1.2 Use a smaller sample volume.

8.2.2 The sample cannot be filtered, diluted, or concentrated prior to analysis without compromising the integrity of the results.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method detection limit (MDL): Refer to current MDL limits.

9.2 Method precision: Refer to current SPC limits.

9.3 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

Not applicable

11.0 ANALYST VERIFICATION

Before a technician/analyst is allowed to analyze samples without supervision, he/she will be trained by qualified personnel. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data is obtained, it is recorded in the alkalinity logbook. When the analysis is complete, the results are entered into ALPHA LIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDS forms are maintained in the laboratory.

13.3 Use care when handling concentrated forms of sulfuric acid.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Beakers: Capacity of 150 mL required

15.2 Graduated cylinders: Minimum capacity of 100 mL is needed

15.3 Magnetic stir plate

15.4 Stir bar

15.5 Magnetic stir bar retriever

15.6 Squeeze bottle for deionized water

15.7 Hot plate

15.8 Buret with a minimum of 0.5 mL increments: Recommended capacity - 10 mL to 20 mL

15.9 Watch glass

15.10 pH meter and probe

15.11 Oven capable of maintaining 250 ± 50° C

NOTE: The temperature of the oven is monitored in accordance with GL-LB-E-004.

15.12 Volumetric flask, 1 L

15.13 Aluminum weigh boat

15.14 Desiccator and desiccant

15.15 Analytical balance: Capable of weighing to 0.0001 g

NOTE: Balances are calibrated in accordance with GL-LB-E-002 for Balances.

16.0 REAGENTS

16.1 Reagents

16.1.1 Sodium Carbonate (Na_2CO_3)

16.1.2 Sulfuric Acid (H_2SO_4)

16.1.3 ASTM type II deionized water

16.1.4 pH buffers

16.1.4.1 pH = 4

16.1.4.2 pH = 7

16.1.4.3 pH =10

16.1.5 Sodium Borate ($Na_2B_4O_7 \bullet 1OH_2O$)

16.2 Solutions

16.2.1 0.05 N sodium carbonate solution (Na_2CO_3)

16.2.1.1 Dry 3 - 5 g of Na_2CO_3 in an oven at 250 ± 50° C for 4 hours.

16.2.1.2 Remove the Na_2CO_3 from the oven and cool in a desiccator.

16.2.1.3 Weigh 2.5 ± 0.2 grams of the dried Na_2CO_3 and transfer to a one-liter volumetric flask.

NOTE: Record the weight of the Na_2CO_3 to the nearest mg in the standardization logbook. The weight is needed in the standardization of the sulfuric acid titrant.

16.2.1.4 Bring to volume with deionized water and mix well.

16.2.1.5 Discard after one week.

16.2.2 0.1 N sulfuric acid titrant

16.2.2.1 Transfer 3.0 mL of concentrated sulfuric acid to a one-liter volumetric flask.

16.2.2.2 Bring to volume with deionized water.

16.2.3 Standardization of the 0.1 N sulfuric acid titrant

NOTE: This must be done monthly

16.2.3.1 Transfer 40.0 mL of 0.05 N sodium carbonate to a 250 mL beaker.

16.2.3.2 Add 60 mL of deionized water.

16.2.3.3 Put a stir bar in the beaker and place on a stir plate.

16.2.3.4 Measure the pH of the solution.

NOTE: Refer to the GL-GC-E-008 for pH.

16.2.3.5 Fill a buret with the 0.1 N sulfuric acid solution.

16.2.3.6 Record the initial volume of titrant in the standardization log.

16.2.3.7 Using the sulfuric acid solution as the titrant, titrate the sodium carbonate solution to a pH of approximately 5. Record the volume of titrant used.

16.2.3.8 Remove the beaker from the stir plate.

16.2.3.9 Place a watch glass over the beaker and put the beaker on a hot plate.

16.2.3.10 Boil the solution gently for 3 - 5 minutes.

16.2.3.11 Cool to room temperature.

16.2.3.12 Rinse any moisture or residue on the watch glass into the same beaker of Na_2CO_3.

16.2.3.13 Titrate the Na_2CO_3 solution again with the H_2SO_4 titrant until a pH of 3.7 is reached.

16.2.3.14 Record the volume of titrant used in the standardization logbook.

16.2.3.15 Calculate the exact normality of the sulfuric acid solution using this formula:

$$\text{Normality of the } H_2SO_4 \text{ solution} = \frac{A \times B}{53.00 \times C}$$

Where:
A = grams of Na_2CO_3 used in preparing Na_2CO_3 solution (refer to 16.2.1.3)
B = volume in mL of the Na_2CO_3 solution transferred to the beaker (refer to 16.2.3.1)
C = total volume of the 0.1 N H_2SO_4 acid titrant used to reach a pH of 3.7

16.2.4 0.02 N sulfuric acid

16.2.4.1 Dilute 200 mL of the 0.1 N sulfuric acid to one liter with DI water.

16.2.5 Standardization of the 0.02 N sulfuric acid

16.2.5.1 Standardize the sulfuric acid solution monthly.

16.2.5.2 Transfer 15.0 mL of 0.05 N Na_2CO_3 solution to a 250 mL beaker.

16.2.5.3 Add 85 mL of deionized water.

16.2.5.4 Put a stir bar in the beaker and place on a stir plate.

16.2.5.5 Measure the pH of the solution.

NOTE: Refer to GL-GC-E-008 for pH.

16.2.5.6 Fill a buret with the 0.02 N sulfuric acid solution.

16.2.5.7 Record the initial volume of titrant in the standardization log.

16.2.5.8 Using the sulfuric acid solution as the titrant, titrate the sodium carbonate solution to a pH of approximately 5. Record the volume of titrant used.

16.2.5.9 Remove the beaker from the stir plate.

16.2.5.10 Place a watch glass over the beaker and put the beaker on a hot plate.

16.2.5.11 Boil the solution gently for 3 - 5 minutes.

16.2.5.12 Cool to room temperature.

16.2.5.13 Rinse any moisture or residue on the watch glass into the same beaker of Na_2CO_3.

16.2.5.14 Titrate the Na_2CO_3 solution again with the H_2SO_4 titrant until a pH of 3.7 is reached.

16.2.5.15 Record the volume of titrant used in the standardization logbook.

16.2.5.16 Calculate the exact normality of the sulfuric acid solution using this formula:

$$\text{Normality of the } H_2SO_4 \text{ solution} = \frac{A \times B}{53.00 \times C}$$

Where:
A = grams of Na_2CO_3 used in preparing Na_2CO_3 solution (refer to 16.2.1.3)
B = volume in mL of the Na_2CO_3 solution transferred to the beaker (refer to 16.2.5.2)
C = total volume of the 0.02 N H_2SO_4 acid titrant used to reach a pH of 3.7

16.2.6 Add Sodium borate LCS.

16.2.6.1 Weigh 3.814 g of Sodium borate • 10 hydrate ($Na_2B_4O_7 \bullet 10H_2O$) into a 1000 mL volumetric flask. Dilute to volume with DI water. Discard after six months.

17.0 PREPARATION OF SAMPLES

Not applicable

18.0 PREPARATION OF STANDARDS

Not applicable

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

Refer to GL-GC-E-008 for pH.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC:

20.1.1 Matrix duplicate is analyzed for every batch of $\leq$ 10 samples and for each set of ten samples in batches with > 10 samples.

20.1.2 LCS is analyzed with each alkalinity batch of $\leq$ 10 samples. Recovery must be 100% ± 10%.

20.1.3 Prepare LCS by diluting 5 mls of Sodium borate solution (16.2.6) to 100 mls with DI water. Analyze as if it were a sample.

20.1.4 A matrix spike (MS) is prepared with each alkalinity batch of $\leq$ 10 samples. Add 5 mls of LCS (Sodium borate) solution to 95 mls of sample. Recovery must be 100% ± 10%.

20.2 Acceptance limits:

20.2.1 Matrix relative percent difference (RPD): Refer to current control charts.

21.0 RUN SEQUENCE

21.1 Samples 1 through x where $x \leq 10$

21.2 Sample x duplicate

22.0 PROCEDURE

22.1 Analysis:

22.1.1 Calibrate the pH meter as described in GL-GC-E-008 for pH.

22.1.2 Record the batch number, matrix, initials, date, and time of analysis in the alkalinity logbook.

22.1.3 Using a graduated cylinder, transfer 100 mL of sample to a 150 mL beaker.

22.1.4 Record the client ID, sample ID, and the volume of sample used in the appropriate columns of the alkalinity logbook.

22.1.5 Measure the pH of the sample. (Refer to the GL-GC-E-008 for pH.)

22.1.6 Record this initial pH in the alkalinity logbook.

22.1.7 Fill the buret with one of the standardized H_2SO_4 titrants and record the normality of the chosen titrant in the alkalinity logbook.

22.1.7.1 Use 0.02 N H_2SO_4 if the alkalinity is expected to be < 1000 mg/L $CaCO_3$.

22.1.7.2 Use 0.1 N H_2SO_4 if the alkalinity is expected to > 1000 mg/L $CaCO_3$

22.1.8 Record the initial volume of the H_2SO_4 acid titrant in the appropriate column of the alkalinity logbook.

22.1.9 Titrate the sample with the H_2SO_4 titrant until the appropriate endpoint is obtained

22.1.9.1 Phenolphthalein alkalinity: Endpoint = pH of 8.3

22.1.9.2 Total alkalinity: Endpoint = pH of 4.5

22.1.10 Record the final volume of the titrant and the total volume of titrant used (final volume - initial volume) in the appropriate columns of the alkalinity logbook.

22.1.11 Repeat steps 22.1.4 - 22.1.10 for each sample and quality control sample in the batch.

22.2 Calculation/reporting of results:

22.2.1 Calculate the total alkalinity using this formula:

$$\text{alkalinity in mg/L} = \frac{Vt \times N \times 50000}{Vs} \quad \text{where}$$

Vt = volume in mL of H_2SO_4 used to reach the pH 4.5 endpoint
N = normality of the H_2SO_4 titrant
Vs = volume in mL of sample used

22.2.2 Calculation of the phenolphthalein alkalinity (P)

22.2.2.1 Calculate P using this formula

$$P \text{ in mg/L} = \frac{Vt \times N \times 50000}{Vs} \quad \text{where}$$

Vt = volume in mL of H_2SO_4 used to reach the pH 8.3 endpoint
N = normality of the H_2SO_4 titrant
Vs = volume in mL of sample used

22.2.3 Calculation of carbonate, bicarbonate, and hydroxide alkalinity.

22.2.3.1 These forms of alkalinity are calculated using the calculations found in Standard Methods, 19th Edition, Method 4500-CO_2D.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Refer to the GL-GC-E-008 for pH for shutdown procedures.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for General Chemistry Data Review and Validation.

25.0 DATA TRANSMITTAL

When a batch is given General Chemistry departmental "DONE" status, it is automatically transferred via ALPHALIMS to reporting personnel.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to GL-GC-E-008 for pH for instrument maintenance.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

29.1 Method detection limit studies are performed in accordance with GL-LB-E-001 for Method Detection Limits

29.2 EPA Method 310.1 states that for a sample with a total alkalinity concentration of < 20 mg/L, the analyst should titrate the sample to pH in the range of 4.3 to 4.7 and the amount of titrant and pH recorded. The pH is then lowered exactly 0.3 pH units and the volume of titrant required to do this recorded. In this SOP, all samples being tested for total alkalinity are titrated to pH of 4.5 regardless of the alkalinity concentration.

29.3 EPA method 310.1 states that analysis should begin as soon as it is practical. This SOP allow 14 days from the date of collection until the start of analysis in accordance with the holding time listed in the Federal Register Volume 49 Number 209 Part 136.3 Table II.

30.0 REFERENCES

30.1 Methods of Chemical Analysis of Water and Wastes. Alkalinity. EPA 600/4 -79-020. Method 310.1 (1979).

30.2 Standard Methods for the Examination of Water and Wastewater 18th Edition. Method 2320 B. Alkalinity Titration Method.

30.3 Federal Register 40 CFR Part 136 "Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act", April 4, 1995.

30.4 Standard Methods for the Examination of Water and Wastewater, 19th Edition, Method 4500-CO_2D, Carbon Dioxide and Forms of Alkalinity by Calculation.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

TOTAL, TOTAL INORGANIC, AND TOTAL ORGANIC CARBON (TOC) USING THE O-I-ANALYTICAL MODEL 1010 TOC ANALYZER

(GL-GC-E-093 REVISION 4)

APPLICABLE TO METHODS:
EPA Method 415.1, EPA SW-846 Method 9060

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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL, TOTAL INORGANIC, AND TOTAL ORGANIC CARBON (TOC) USING THE OI-ANALYTICAL MODEL 1010 TOC ANALYZER

2.0 METHOD CODE

2.1 EPA Method 415.1

2.2 EPA SW-846 Method 9060

3.0 METHOD OBJECTIVE/PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to describe the procedure used to run samples for total, total inorganic, and total organic carbon using the O-I Analytical Model 1010 TOC analyzer.

4.0 METHOD SUMMARY

4.1 Total organic carbon is converted to carbon dioxide by chemical oxidation of the organic carbon in the sample. The carbon dioxide is measured using a non-dispersive infrared detector.

4.2 Synonym: Non-purgeable organic carbon

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid or solid samples. In these cases, the procedure is modified as necessary.

NOTE: SC DHEC requires analysis by SW846 9060 if samples are not drinking water or wastewater and the data is to be used for regulatory purposes.

6.0 HOLDING TIME

Holding time is 28 days from the time and date of collection until the start of analysis unless otherwise specified.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Storage of samples in amber glass bottles is preferred. Polyethylene bottles may be used if blanks are collected to show that the containers do not contaminate the samples.

7.2 Unless samples are to be analyzed within two hours of collection, they should be acidified to a pH of two or less with H_2SO_4.

7.3 Samples should be stored at 4 ± 2° C.

7.4 If the concentration of dissolved organic carbon is to be determined, samples should be filtered through a 0.45 um filter at the time of collection.

8.0 INTERFERENCES

Carbonates and bicarbonates must be removed before analysis for TOC.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 0.2 - 20 mg/L with the sample loop set at 5 mL loop size.

9.2 Calibration range: 0.2-20 mg/L.

9.3 Method detection limit (MDL): Refer to current MDL study.

9.4 Method precision: Refer to current SPC limits.

9.5 Method accuracy: Refer to current SPC limits.

10.0 DEFINITIONS

10.1 Laboratory Control Sample (LCS) - A standard, usually of the same matrix as the sample batch being organized, taken through the same prep process as the samples, then analyzed with the batch.

10.2 Total Organic Carbon - All carbon in a sample besides carbonates and bicarbonates.

10.3 Non-purgeable Organic Carbon - All organic carbon that is not removed by sparging.

10.4 Total Carbon - Total amount of carbon in a sample.

10.5 Total Inorganic Carbon – All inorganic carbon in a sample that is separated from organic carbon by acidification.

10.6 Dissolved Organic Carbon- All organic carbon in a sample that has been filtered through a 0.45 micron filter.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

12.1 As data is obtained, computer printouts of the data are generated. These dated hard copies of the data are stored in the TOC-1010 binder. Results are uploaded into the laboratory information management system.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDS forms are maintained in the laboratory.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 I-O Analytical Model 1010 TOC Analyzer including:

15.1.1 Reaction module

15.1.2 Detector/electronics module

15.1.3 Printer module

15.1.4 Autosampler module

15.2 Compressed nitrogen (zero grade) and two stage regulator

15.3 Flow meter

15.4 Personal computer (for entering data)

16.0 REAGENTS

16.1 Raw materials: (Chemicals should be at least ACS grade or equivalent)

16.1.1 Potassium acid phthalate, $KHC_8H_4O_4$

16.1.2 Concentrated phosphoric acid, H_3PO_4 (85%)

16.1.3 5% (by volume) Phosphoric acid reagent,

Dilute 59mls of H_3PO_4 (85%) to 1000ml using DI H_2O.

16.1.4 ASTM Type II deionized water.

16.1.5 Sodium bicarbonate, $NaHCO_3$

16.2 Persulfate reagent:

Dissolve 100 g sodium persulfate in a 1 liter volumetric flask using deionized (DI) water.

Bring to volume with DI water.

17.0 PREPARATION OF SAMPLES

Not applicable.

18.0 PREPARATION OF STANDARDS AND QUALITY CONTROL SAMPLES

18.1 Standards are prepared according to the recipes found in ALPHALIMS.

Standards are stored in the Reagent Cabinet.

Stock standards are stored in amber bottles and are good for six months.

18.2 Documentation of standards and their preparation are maintained in ALPHALIMS in accordance with GL-LB-E-007 "Laboratory Standards Documentation."

18.3 Laboratory Control Sample(s) (LCS): The LCS is prepared by spiking an aliquot of DI water with the TOC stock standard solution.

18.3.1 The LCS is made up daily from 2nd source standard.

18.4 Calibration standards: The concentrations used are listed below:

20.0 mg/L
10.0 mg/L
1.00 mg/L
0.20 mg/L
0.0 mg/L

18.4.1 Calibration standards are made up daily from 1° stock standard.

18.5 Initial Calibration Verification (ICV): The ICV is a 10.0 mg/L standard made from the second source stock standard. The ICV must be run immediately after the calibration standards.

18.6 Continuing Calibration Verification (CCV): The CCV is a 10.0 mg/L standard made from the same source stock standard as the calibration standards. A CCV must be run after every 10 samples and after the last sample in the run.

18.7 Total Inorganic Carbon (TIC) Check standard: This standard is analyzed once per run to ensure that the instrument is adequately removing inorganic carbon.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

19.1 Refer to Chapter 4: Operation of the O-I Model 1010 Wet Oxidation Total Organic Carbon Analyzer Operator's Manual.

19.2 Before a run is started, make sure there is an adequate amount of sodium persulfate reagent to complete the analysis.

19.3 Prior to the start of analysis, ensure that the nitrogen flow is between 40 and 60 psi.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Instrument QC

20.1.1 An initial calibration verification (ICV) is analyzed immediately after the calibration standards. This standard must be made from a different source than the calibration standards.

20.1.2 An initial calibration blank (ICB) is analyzed following the ICV.

A continuing calibration verification (CCV) is analyzed after every 10 analytical samples and after the last analytical sample in the run.

A continuing calibration blank (CCB) is analyzed after every CCV.

A TIC check standard is immediately after the ICB.

20.2 Batch QC

20.2.1 A matrix spike and a matrix duplicate are analyzed for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples (unless otherwise required by client contract).

A method blank and laboratory control sample (LCS) are analyzed at least once for every batch of 20 samples or less.

For liquid samples, the LCS is normally a 10 mg/L standard taken through the same process as the samples.

LCS duplicates are analyzed if required by client contract.

20.3 Acceptance limits:

20.3.1 Correlation coefficient must be 0.995 or greater.

20.3.2 ICV recovery must be 90-110% for all batches (unless otherwise specified by client contract). If not, the ICV should be remade and reanalyzed. If the ICV continues to be out of range, the primary calibration standard should be remade and reanalyzed.

CCV recovery must be 90-110% for all batches (unless otherwise specified by client contract). If the CCV continues to be out of range, the instrument must be recalibrated.

Matrix relative percent difference (RPD): Refer to current SPC limits

Matrix spike recovery: Refer to current SPC limits.

Method blank: Must be less than the CRDL.

LCS: Refer to current SPC limits.

LCS RPD: Refer to current SPC limits.

If analysis by EPA Method 415.1 is requested, the samples are analyzed in duplicate. The Relative Percent Difference (RPD) between the two values must be ≤ 20% when the values are greater than 5 mg/L.

If analysis by SW-846 9060 is requested, samples are analyzed quadruplicate. The Relative Percent Difference (RPD) between the two values must be ≤ 20% when the values are greater than 5 mg/L.

The TIC check standard is acceptable if the concentration of total organic carbon determined from its analysis is less than the 0.5 mg/L.

20.4 Handling out-of-control situations:

20.4.1 If a sample result exceeds the concentration of the highest calibration standard, the sample must be diluted appropriately with DI water and reanalyzed.

20.4.2 The correlation coefficient must be at least 0.995. If it is less than 0.995 the calibration standards must be reanalyzed. Analysis of samples cannot begin until a correlation coefficient of 0.995 is obtained.

21.0 RUN SEQUENCE

21.1 Calibration standards, including DI Blank

21.2 ICV

21.3 ICB

21.4 TIC check standard

21.5 Up to 10 analytical samples including LCS, Method Blank, and sample QC (refer to Section 20)

21.6 CCV (Continuing Calibration Verification)

21.7 CCB

21.8 Repeat steps 21.5 – 21.7 for remaining samples in the run ending with CCV and CCB.

22.0 PROCEDURE

22.1 Analysis: Refer to Chapter 4 (pages. 62-71), Operation of the Model 1010 Wet Oxidation Total Organic Carbon Analyzer Operator's Manual.

22.2 Calculation/reporting of results:

22.2.1 As the data is obtained; it is uploaded into ALPHALIMS.

22.2.2 If a sample is analyzed by EPA 415.1, the average of the two replicates is reported for the TOC or Total Carbon Concentration.

22.2.3 For samples analyzed by SW 846-9060, all four replicates plus the average are reported for the TOC concentration.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURES

Refer to Chapter 4, page 74, Operation of the Model 1010 Wet Oxidation Total Organic Carbon Analyzer Operator's Manual.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for Data Packaging and Validation.

25.0 DATA TRANSMITTAL

When a batch is given General Chemistry departmental "DONE" status, it is made available to reporting personnel.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to Chapters 5 and 6 of the O-I Model 1010 Wet Oxidation Total Organic Carbon Analyzer Operator's Manual.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

29.1 To ensure accuracy, % error is calculated for the duplicate values of all concentrations greater than 1 mg/L.

29.2 The % error must be 10% or less for samples logged according to Method 415.1. If not, the samples must be reanalyzed.

30.0 REFERENCES

30.1 Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, "Organic Carbon, Total", Method 415.1 (Combustion or Oxidation), March 1979.

30.2 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume 1C, SW-846, Third Edition, November 1986. Method 9060, "Total Organic Carbon," Revision 0, September 1996. USEPA Office of Solid Waste and Emergency Response, Washington, DC 20460.

30.3 O-I Analytical Model 1010 Wet Oxidation Total Organic Carbon Analyzer Operator's Manual.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

TOTAL DISSOLVED SOLIDS

(GL-GC-E-001 REVISION 6)

APPLICABLE TO METHODS:
EPA 160.1
Standard Methods 18th Edition. 2540 C

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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL DISSOLVED SOLIDS

2.0 METHOD CODE

2.1 EPA 160.1

2.2 Standard Methods 18th Edition 2540 C

3.0 METHOD OBJECTIVE / PURPOSE

This procedure is used to measure total dissolved solids (TDS) in waters and wastewaters. TDS are those solids capable of passing through a standard glass fiber filter and dried to a constant weight at 180° C.

4.0 METHOD SUMMARY

4.1 Summary: In this gravimetric procedure, a water sample is filtered through a glass fiber filter into a preweighed porcelain crucible. The filtrate is evaporated to dryness and dried to a constant weight at 180° C. The increase in the dish weight represents the total dissolved solids.

4.2 Synonym: Residue, Total Filterable (Dried at 180° C)

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid samples. In these cases, the procedure is modified as necessary.

6.0 HOLDING TIME

Seven days filtration from the time and date of collection unless otherwise specified by contract.

7.0 SAMPLE CONTAINER, PRESERVATION, COLLECTION, STORAGE REQUIREMENTS

7.1 Samples may be stored in glass or plastic containers.

7.2 Preservation:

7.2.1 No preservatives are required. Preserved samples should never be analyzed.

7.2.2 Documentation of temperature and pH are documented at Login. Refer to GL-SR-E-001 for Sample Receipt, Login, and Storage.)

7.3 Refrigerate sample at 4° ± 2° C until analysis to minimize microbiological decomposition of solids.

8.0 INTERFERENCES

8.1 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.

8.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180° C to ensure that all the bicarbonate is converted to carbonate.

8.3 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.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 10 mg/L to 20,000 mg/L

9.2 Method detection limit (MDL): Refer to current MDL study

9.3 Method precision: Refer to SPC limits

9.4 Method accuracy: Refer to SPC limits

10.0 DEFINITIONS

10.1 Hygroscopic - Attracting, absorbing, and retaining atmospheric moisture.

10.2 Gravimetric - Pertaining to measurement by weight.

10.3 Desiccant - Material used to absorb moisture present.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon the successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data is obtained, it is recorded in AlphaLIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDS forms are maintained in the laboratory.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION / EQUIPMENT / GLASSWARE

15.1 Analytical balance, capable of weighing to 0.0005g.

NOTE: The balance must be calibrated in accordance with the procedure outlined in the GL-LB-E-002 for Balances.

15.2 Drying oven, for operation at 180° ± 2° C.

15.3 Drying oven for operation at approximately 100° C. (Optional)

15.4 Desiccator with a color-indicating desiccant.

15.5 Porcelain crucibles, 100 ml capacity or larger.

15.6 Glass fiber filter paper, 4.7 cm.

15.7 Filtration flask. (Minimum size is 250 mL)

15.8 Magnetic filter funnel.

15.9 Tongs.

15.10 Vacuum source.

15.11 Graduated cylinders. (Typical capacity required is 100 mL.)

15.12 Thermometers are calibrated in accordance with GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators, and other Similar Devices, and capable of recording temperatures up to 182° C.

16.0 REAGENTS

16.1 Sodium chloride, NaCl

16.2 ASTM Type II Deionized Water

17.0 PREPARATION OF SAMPLES

Not Applicable

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards and their preparation is kept in maintained in AlphaLIMS in accordance with to GL-LB-E-007 for standards documentation.

18.2 Laboratory control sample(s) (LCS): 300 mg/L sodium chloride, NaCl. Weigh 0.300 g of NaCl and dilute to 1000 mL with deionized water.

The LCS should be discarded after six months.

19.0 INSTRUMENT / EQUIPMENT START-UP PROCEDURES

19.1 Preparation of desiccators:

19.1.1 Ensure that the desiccant is activated by observing the blue color indicator. **NOTE**: If < 50% of the indicator desiccant is blue, change the desiccant.

19.1.2 Desiccator must be sealed. Any moisture absorbed by the crucibles can cause erroneous results.

19.1.3 Label desiccators to be used with the date and what they will contain.

19.2 Preparation of crucibles:

19.2.1 Crucibles are cleaned by the glassware technicians, according to GL-LB-E-003 for Glassware Preparation, and stored in a drying oven.

19.2.2 Crucibles are marked by the analyst with a grease pencil and identified with a letter and/or a number.

19.2.3 The analyst is responsible for the preparation of the crucibles as follows:

19.2.3.1 Place cleaned crucibles in the drying oven at 180 ± 2° C.

19.2.3.2 Set the temperature at or 180° C.

19.2.3.3 Crucibles should remain at the specified temperature for a minimum of one hour.

NOTE: The oven/furnace temperature should not be allowed to drop below 100° C before the crucibles are removed and placed in desiccators.

19.2.3.4 Using tongs, remove the crucibles from the oven or furnace and place in a desiccator immediately.

19.2.3.5 Allow crucibles to cool in desiccators to room temperature before use. If it is possible, allow crucibles to cool for at least 12 hours.

19.3 Filter Papers (if prewashed, certified filters are being used, no filter preparation is needed):

19.3.1 Place glass fiber filter in filter apparatus.

19.3.2 Rinse with 100 mL of deionized water.

19.3.3 Apply vacuum until water is removed from the filter.

19.3.4 Place the filter in an oven to dry at approximately 100° C and store in a desiccator until needed.

NOTE: If necessary, the filter can be washed just prior to use and can be used without drying in an oven.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC:

20.1.1 A matrix duplicate should be analyzed for every batch of ≤ 10 samples and for each set of ten samples in batches with ≥ 10 samples.

20.1.2 A method blank and laboratory control sample (LCS) should be analyzed once for every batch containing ≤ 20 samples.

NOTE: LCS duplicates are analyzed if required by contract or requested by client or if matrix QC is not available

20.2 Acceptance limits:

20.2.1 Matrix relative percent difference (RPD): Refer to current SPC limits.

20.2.2 Method Blank: less than the CRDL.

20.2.3 LCS: Refer to current SPC limits.

20.4 Handling out-of-control situations:

20.4.1 Notify the group leader or team task leader immediately.

20.4.2 If the LCS, LCS RPD, matrix RPD, or blanks fall outside of current acceptance limits, the samples to which the unacceptable QC pertains must be reanalyzed.

20.4.3 The analyst should document in case narrative for the batch the specific QC that is out-of-control and cross-reference data from any subsequent reanalysis.

21.0 SUGGESTED RUN SEQUENCE

21.1 Samples 1 through x where x ≤ 10

21.2 Sample x duplicate

21.3 Method blank

21.4 Repeat steps 21.1 - 21.3 for every group of ten samples in the batch.

21.5 LCS

22.0 PROCEDURE

22.1 Calibration of equipment/instrumentation:

22.1.1 Balance

22.1.1.1 Ensure that the analytical balance to be used has been calibrated and is within control limits before use. Refer to the balance logbook and GL-LB-E-002 for balances, for limits.

22.1.1.2 Check and document, in the logbook provided, the calibration of the balance before use. Refer to GL-LB-E-002 for balances.

22.1.2 Oven

22.1.2.1 Make sure that the oven to be used is at a temperature that is within acceptance limits.

22.1.2.2 Control limits for the drying oven are documented on the temperature log.

22.1.2.3 The oven temperature log format provides the required documentation to ensure that the oven temperature was in control during the drying process.

22.1.2.4 Refer to GL-LB-E-004 for Temperature Monitoring.

22.2 Analysis:

22.2.1 Remove the prepared crucibles from the desiccator.

NOTE: Crucible should be removed from the desiccator just immediately prior to weighing.

NOTE: NEVER touch the crucibles with your hands. Always use tongs or kimwipes.

22.2.2 Record the crucible ID, sample number, and the weight of each crucible to be used in AlphaLIMS in the appropriate columns.

22.2.3 Place a prepared glass fiber filter in the filter apparatus.

22.2.4 Thoroughly mix the sample to be analyzed.

22.2.5 Filter the sample through the glass fiber filter into a clean filter flask. Volume of filtrate needed is 100 mL.

22.2.6 Allow the vacuum pump to remain on after filtration to remove as much water as possible. (Approximate time required is 2-3 minutes.)

22.2.7 Measure a 100 mL aliquot of the filtrate with a clean graduated cylinder and transfer it to the designated preweighed crucible.

NOTE: Volume of filtrate used may vary depending upon the matrix of the sample.

22.2.8 Place the crucible and filtrate in an oven at 180 ± 2°C until the filtrate evaporates to dryness. If the analyst feels there will be a problem putting the crucible and filtrate directly into the 180 ± 2°C oven such as splattering, the crucible and filtrate may first be placed in an oven at 100°C until the filtrate evaporates to dryness.

22.2.9 Continue to dry for a minimum of 1 hour in an oven at 180 ± 2° C. CAUTION: The temperature of the oven must be recorded or results may be considered invalid.

22.2.10 Rinse the used funnel thoroughly before beginning to filter the next sample.

22.2.11 Repeat steps 22.2.3-22.2.10 for all samples, blanks, duplicates, and LCS to be analyzed.

22.2.12 Using tongs to remove the crucibles from the oven and cool to room temperature in a desiccator.

22.2.13 Weigh and record the weight of each crucible in AlphaLIMS in the appropriate column.

22.2.14 Put the crucibles back into an oven at 180± 2° C for a minimum of one hour.

22.2.15 Repeat 22.2.12-22.2.14 until a constant weight is obtained. Constant weight is defined by EPA 160.1 as weight loss or gain of .0005 g.

22.3 Calculation/reporting of results:

22.3.1 Calculate TDS as follows:

$$\text{TDS, mg/L} = \frac{(A-B) \times 1000000}{C}$$

A= final weight of dried residue + crucible (in grams)
B = initial weight of crucible (in grams)
C = volume of filtrate used (in mL)

22.3.2 Results are reported in mg/L.

22.3.3 LCS recoveries are calculated as follows:

$$\frac{\text{Actual [TDS] mg/L obtained}}{\text{Known [TDS] mg/L}} \times 100$$

22.3.4 RPDs are calculated as follows:

$$\frac{\text{[TDS mg/L] sample - [TDS mg/L] duplicate}}{\text{Average [TDS mg/L] of the sample + duplicate}}$$

23.0 INSTRUMENT AND EQUIPMENT SHUT-DOWN PROCEDURES

Not Applicable

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURES

Refer to GL-GC-E-092 for Data Packaging and Validation.

25.0 DATA TRANSMITTAL

When a batch is given General Chemistry departmental "DONE" status, the data is automatically available to reporting personnel.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT / EQUIPMENT MAINTENANCE

27.1 Ovens and Thermometers

27.1.1 Refer to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators, and other Similar Devices.

27.2 Balance

27.2.1 Refer to GL-LB-E-002 for Balances.

27.3 Procedure for maintenance of desiccant

27.3.1 Analysts are responsible for ensuring that the desiccators are maintained by replacing the desiccant whenever 50% of the blue indicator starts to turn pink.

27.3.2 Dry desiccant for reuse as follows:

27.3.2.1 Spread desiccant out in an aluminum pan.

27.3.2.2 Place in drying oven capable of maintaining 105° C for one hour or more.

27.3.2.3 Remove from oven.

NOTE: All desiccants should be blue. If not, discard the dessicant.

27.3.2.4 Place in a desiccator immediately to cool.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper handling and disposal of all types of wastes from this procedure, refer to GL-LB-G-001, the Laboratory Waste Management Plan.

29.0 METHOD VERIFICATION

29.1 Step 19.3.2 differs from the method. The method mentions three 20 mL rinses of the filter paper with deionized water. As written, this SOP asks for the filter papers to be rinsed only once with 100 mL of deionized water.

29.2 MDLs are calculated in accordance with GL-LB-E-001 for Determination of Method Detection Limits.

29.3 Methods SM2540C and EPA 160.1 require that the filtrate be evaporated in a steam bath before being dried at 180° C. This SOP replaces the steam bath with an oven at 100° C. This oven is only used if the analyst feels there will be a problem placing the sample directly in the 180°C oven when liquid is present.

30.0 REFERENCES

30.1 Federal Register 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act," April 4, 1995

30.2 Manual of Methods For Chemical Analysis of Water and Wastes. US EPA Technology Transfer, EPA-625/6-74-003a, 1976

30.3 Methods for Chemical Analysis of Water and Wastes EPA 600/4-79-020. March 1979. Method 160.1, "Total Dissolved Solids."

30.4 Standard Methods for the Examination of Water and Wastewater, 18th Edition. Method 2540 C.

30.5 Compilation of ASTM Standard Definitions, sponsored by ASTM Committee on Terminology. 7th Edition, American Society for Testing and Materials 1990.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

TOTAL SUSPENDED SOLIDS

(GL-GC-E-012 REVISION 5)

APPLICABLE TO METHODS:

EPA 160.2
Standard Methods 18th Edition 2540 D

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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL SUSPENDED SOLIDS

2.0 METHOD CODE

2.1 EPA 160.2

2.2 Standard Methods 18th Edition 2540 D

3.0 METHOD OBJECTIVE/PURPOSE

This procedure is used to measure total suspended solids (TSS) in waters and wastewaters. TSS are those solids that are retained by a standard glass fiber filter and dried to a constant weight at 103 - 105° C.

4.0 METHOD SUMMARY

4.1 Summary: In this gravimetric procedure, a water sample is filtered through a preweighed glass fiber filter. The filter is then dried to a constant weight at 103 - 105° C. The weight of the residue on the filter represents the total suspended solids.

4.2 Synonym: Residue, total non-filterable

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

NOTE: Clients may request that this analysis be performed on miscellaneous liquid samples. In these cases the procedure is modified as necessary.

6.0 HOLDING TIME

Holding time is seven days from the time and date of collection until the start of analysis unless otherwise specified by contract.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples may be stored in glass or plastic containers.

7.2 No preservatives are required. Preserved samples should not be analyzed.

7.3 Nonhomogeneous particles such as leaves, sticks, fish, and lumps of fecal material should be excluded from the sample.

7.4 Refrigerate samples at 4 ± 2° C until the start of analysis to minimize microbiological decomposition of solids.

8.0 INTERFERENCES/LIMITATIONS

8.1 Too much residue on the filter will entrap water and may require prolonged drying.

8.2 For samples that are high in dissolved solids, thoroughly wash the filter to ensure the removal of the dissolved material.

8.3 Prolonged filtration times resulting from filter clogging may produce high results due to the excessive capture of solids on the clogged filter.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 4 mg/L - 20,000 mg/L

9.2 Method detection limit (MDL): Refer to current MDL study

9.3 Method precision: Refer to current SPC limits

9.4 Method accuracy: Refer to current SPC limits

10.0 DEFINITIONS

10.1 Hygroscopic - Attracting, absorbing, and retaining atmospheric moisture.

10.2 Gravimetric - Pertaining to measurement by weight.

10.3 Desiccant - Material used to absorb moisture.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

As data is obtained, it is recorded in the TSS logbook. When the analysis is complete, the results are uploaded into ALPHA LIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNING

13.1 Wear eye protection with side shields while performing procedures in the lab.

13.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS.) These documents and client sample MSDS forms are maintained in the laboratory.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Analytical balance capable of weighing to 0.1 mg.

NOTE: The balance must be calibrated in accordance with the procedure outlined in GL-LB-E-002 for Balances.

15.2 Drying oven for operation at 103 - 105° C.

15.3 Desiccator with a color indicating desiccant.

15.4 Glass fiber filter paper, 4.7 cm

NOTE: If filters are not certified to be pre-washed they must be prepared according to step 19.2.

15.5 Filtration flask (minimum size: 250 mL)

15.6 Magnetic filter funnel

15.7 Tweezers

15.8 Vacuum source

15.9 Graduated cylinders (typical capacity required: 100 and 500 mL)

15.10 Thermometer calibrated according to GL-QS-E-007 for Thermometer Calibration and capable of measuring temperatures of 103 - 105° C.

15.11 Aluminum weigh boats

15.12 Volumetric flask (100 mL capacity)

16.0 REAGENTS

16.1 ASTM Type II deionized water (DI)

16.2 Desiccant

16.3 Celite

17.0 PREPARATION OF SAMPLES

Not Applicable

18.0 PREPARATION OF STANDARDS

18.1 500 mg/L Celite standard.

NOTE: This standard serves as the LCS.

18.2 Add 0.0500 g of Celite to a 100 mL volumetric flask that is partially filled with DI water.

18.3 Bring to volume with deionized water. Mix well.

18.4 Prepare a separate standard for each LCS and LCS duplicate.

18.5 Document preparation of standards in the TSS Standards logbook according to GL-LB-E-007 for Laboratory Standards Documentation and GL-GC-E-004 for Standards Definition and Preparation.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

19.1 Preparation of desiccators:

19.1.1 Ensure that the desiccant is activated by observing the blue color indicator.

NOTE If < 50% of the indicator desiccant is blue, change the desiccant.

19.1.2 Desiccator must be sealed. Any moisture absorbed by the filters can cause erroneous results.

19.1.3 Label desiccators to be used. Include the date that the desiccant was changed and what will be stored in the desiccator.

Filter papers

NOTE: If pre-washed filter papers are being used, proceed to step 22):

19.2.1 Place a glass fiber filter in the filter apparatus.

19.2.2 Rinse with 100 mL of DI water.

19.2.3 Apply vacuum until the water is removed from the filter.

19.2.4 Place the filter on aluminum foil in an oven to dry at 103 - 105° C for one hour.

19.2.5 Store the washed filter in a desiccator.

19.2.6 Alternatively, prewashed filters may be used as purchased.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Frequency of QC:

20.1.1 A method blank and matrix duplicate are analyzed for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples.

20.1.2 A laboratory control sample is analyzed for every batch containing ≤ 20 samples.

NOTE: An LCS duplicate is analyzed per client request.

20.2 Acceptance limits:

20.2.1 Matrix relative percent difference (RPD): Refer to current SPC limits

NOTE: If the difference between the sample concentration and duplicate concentration is less than or equal to 5, the results are acceptable even though the RPD may exceed current SPC limits.

20.2.2 Method blank: - CRDL $\leq$ method blank $\leq$ CRDL

20.2.3 LCS: Refer to current SPC limits

20.2.4 LCS RPD: Refer to current SPC limits

20.3 Handling out-of-control situations:

20.3.1 Notify the group leader immediately.

20.3.2 If the matrix or LCS RPD, blank, and/or LCS recovery fall outside of current acceptance limits, the samples to which the unacceptable quality control (QC) pertains must be reanalyzed.

20.3.3 Document in the TSS logbook the specific QC that is out of control and cross-reference data from any subsequent reanalysis.

21.0 RUN SEQUENCE

21.1 Samples 1 through x where x $\leq$ 10

21.2 Method blank

21.3 Sample *x* duplicate

21.4 Repeat steps 21.1 - 21.3 for every group of 10 samples in the batch.

21.5 LCS

22.0 PROCEDURE

22.1 Calibration of equipment/instrumentation:

22.1.1 Balance

22.1.1.1 Ensure that the analytical balance to be used has been calibrated and it is within control limits before use. Refer to the balance logbook and GL-LB-E-002 for Balance.

22.1.2 Oven

22.1.2.1 Make sure that the oven to be used is at a temperature that is within acceptance limits.

22.1.2.2 Control limits for the drying oven are documented on the temperature log.

22.1.2.3 The oven temperature log format provides the required documentation to ensure that the oven temperature was in control during the drying process.

22.1.2.4 Refer to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators and Other Similar Devices.

22.2 Analysis:

22.2.1 Label an appropriate number of aluminum weigh boats (one per sample).

22.2.2 Remove, immediately prior to weighing, the pre-washed glass fiber filter prepared as described in section 19.0 from the desiccator.

NOTE: **NEVER** touch the filter with your hands. Always use tweezers or tongs.

22.2.3 Record the weigh boat ID, sample number, and the weight of each filter to be used in the appropriate columns in the TSS logbook.

22.2.4 Dry the filters for at least one hour at 103 - 105° C.

22.2.5 Remove the filters from the oven and cool in a desiccator until they reach room temperature.

22.2.6 Weigh each filter and record its weight in the appropriately labeled column of the TSS logbook.

22.2.7 Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained for each filter. Constant weight is defined as a weight loss or gain ≤ 0.5 mg or 0.0005 g.

22.2.8 Place the filter on the filter apparatus.

22.2.9 Thoroughly shake the sample to be analyzed.

22.2.10 Rapidly transfer 100 mL of the sample to the filter by means of a 100 mL graduated cylinder. Record the volume of sample used in the TSS logbook.

NOTE: The volume of sample to be used can be increased or decreased depending upon the matrix of the sample. If there is minimal residue (< 1.0mg) on the filter after filtering 100 mL, an additional 900 mL of sample must be filtered. (Total volume of sample: 1000 mL). In some cases the filter may clog, preventing additional sample from being filtered. If this happens, the analyst must document in the records that a 10-minute filtration time was used to meet the 1.0mg requirement.

NOTE: 500 mL of deionized water must be filtered for the blank.

20.2.11 Apply the vacuum and filter the sample.

20.2.12 Rinse the graduated cylinder three times with DI water and transfer the rinsate to the funnel to ensure that all residue is transferred.

20.2.13 Remove any lingering residue from the funnel by rinsing thoroughly with three successive volumes of deionized water (approximately 10 mL each).

20.2.14 Continue to apply the suction after the filtration is complete in order to remove as much water as possible.

20.2.15 Carefully remove the filter from the filter apparatus.

20.2.16 Repeat steps 22.2.8 - 22.2.15 for each sample or QC sample in the batch.

20.2.17 Dry the filters for at least one hour at 103 - 105° C. If time allows, allow the filter to dry overnight.

20.2.18 Weigh each filter and record its weight in the appropriately labeled column of the TSS logbook.

20.2.19 Repeat the cycle of drying, cooling, desiccating and weighing until a constant weight is obtained for each filter.

NOTE: The amount of residue on the filter should fall in the range of 10-200 mg.

22.3 Calculation/reporting of results:

22.3.1 Calculate TSS as follows:

$$\text{TSS (mg/L)} = \frac{A - B \times 1{,}000{,}000}{C}$$

Where:

A = Final weight of the filter plus residue in grams
B = Weight of the filter paper in grams. (This is the last weight of the filter obtained prior to filtration.)
C = Volume of the sample in mL.

22.3.2 Results are reported in mg/L.

22.3.3 RPDs are calculated as follows:

$$\frac{([\text{TSS mg/L}]\,\text{sample} - [\text{TSS mg/L}]\,\text{duplicate})}{\text{Average}\,[\text{TSS mg/L}]\,\text{of sample and duplicate}} \times 100$$

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Not Applicable

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

Refer to GL-GC-E-092 for General Chemistry Data Packaging and Validation.

25.0 DATA TRANSMITTAL

When a batch is given General Chemistry departmental "DONE" status, the data is automatically available to reporting personnel.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

27.1 Ovens and Thermometers:

27.1.1 Refer to GL-LB-E-004 for Temperature Monitoring and Documentation Requirements for Refrigerators, Freezers, Ovens, Incubators, and other Similar Devices.

27.2 Balances:

27.2.1 Refer to GL-LB-E-002 for Balances.

27.3 Procedure for the maintenance of desiccant:

27.3.1 Analysts are responsible for ensuring that the desiccators are maintained by replacing the desiccant whenever 50% of the blue indicator starts to turn pink.

27.3.2 Dry desiccant for reuse as follows:

27.3.2.1 Spread desiccant out in an aluminum pan.

27.3.2.2 Place in drying oven capable of maintaining 105° C for one hour or more

27.3.2.3 Remove from the oven.

NOTE: All desiccant should be blue.

27.3.2.4 Place in a desiccator immediately to cool.

27.3.2.5 Place a label on the desiccator indicating the day that the desiccant was changed and the next scheduled change.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

29.0 METHOD VERIFICATION

29.1 Step 19.2.2 differs from EPA method 160.2 and SM 2540 D. Both methods mention three 20 mL rinses of the filter paper with deionized water during filter preparation. As written, this SOP asks for the filter papers to be rinsed only once with 100 mL of deionized water.

29.2 Constant weight is defined in EPA 160.2 and SM 2540 D as a weight loss or gain < 4% of the previous weight or 0.0005 g. Constant weight is defined in this SOP as a difference equal to or less than 0.0005 g.

29.3 MDLs are calculated in accordance with GL-LB-E-001 for Determination of Method Detection Limits.

29.4 Step 22.2.10 is in accordance with EPA 160.2 but differs from SM 2540 D, which calls for the pipetting of the sample aliquot to the filter instead of transferring by a graduated cylinder.

30.0 REFERENCES

30.1 Federal Register 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act," April 4, 1995.

30.2 Methods for Chemical Analysis of Water and Wastes. EPA 600/4-79-020, March 1979, Method 160.2, "Residue, Non-Filterable."

30.3 Standard Methods for the Examination of Water and Wastewater, 18th Edition Method 2540 D.

30.4 Compilation of ASTM Standard Definitions. Sponsored by ASTM Committee on Terminology, 7th Edition, Philadelphia, American Society for Testing and Materials, 1990.

30.5 Manual of Methods for Chemical Analysis of Water and Wastes. EPA Technology Transfer, EPA-625/6-74-003a, 1976.

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

ION CHROMATOGRAPHY (IC)

(GL-GC-E-086 REVISION 10)

APPLICABLE TO METHODS:
Standard Method 4110b, 18th Edition
EPA Method 300.0
SW 846 Method 9056

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1.0 STANDARD OPERATING PROCEDURE FOR ION CHROMATOGRAPHY (IC)

2.0 METHOD CODES

2.1 Standard Method 4110-B, 18th Edition

2.2 EPA Method 300.0

2.3 SW-846 Method 9056

NOTE: The basic principles of these methods have been adapted for TATB, which will be reported as a GEL Method.

3.0 METHOD OBJECTIVE/PURPOSE

3.1 This standard operating procedure (SOP) provides necessary instructions for the determination of the following inorganic anions by Ion Chromatography:

Bromide, Bromate, Chloride, Chlorate, Chlorite, Fluoride, Nitrate-N, Nitrite-N, Sulfate, ortho-Phosphate-P, Oxalate, and 1,3,5-triaminotrinitrobenzene (TATB) is also discussed.

NOTE: For EPA Method 314.0 (Perchlorates by IC) see GL-GC-E-096.

3.2 The applicable matrixes to this method are as follows:

3.2.1 Drinking water
3.2.2 Surface water
3.2.3 Ground water
3.2.4 Wastewater
3.2.5 Reagent waters
3.2.6 Solids (after extraction)
3.2.7 Leachates (when no acetic acid is used)

3.3 A small volume of sample is introduced into the Ion Chromatograph (IC). The anions of interest are separated and measured after traveling through a series of columns and a suppressor device. The sample passes through a conductivity detector (CDM) (used for anions) or a variable wavelength detector (VDM) (used for TATB).

3.4 An extraction procedure must be performed to use this method for solids.

3.5 Approximately 4.9 ml of sample for Dionex IC's and 10mls of sample for Metrohm IC's is flushed through the sample loop prior to injecting the sample. The large amount of sample flushing prevents sample cross- contamination.

4.0 METHOD APPLICABILITY

4.1 Method Detection Limit: The MDL is updated and verified every six months.

4.2 Method Precision: The limits are static at 100 ±10%.

4.3 Method Accuracy: See the current SPC limits for these methods.

4.4 Technicians and analysts do not analyze client samples without supervision until they have been fully trained and have demonstrated the ability to generate acceptable data. Training records are maintained as quality records.

5.0 DEFINITIONS

5.1 Calibration Blank - A volume of reagent water without the analytes, internal standards or surrogates used within the calibration curve.

5.2 Calibration Standard (CAL) - A solution prepared from the primary stock solution. The CAL solutions are used to calibrate the instrument.

5.3 Instrument Calibration Verification (ICV) - A solution of the method analytes used to evaluate the performance of the instrument with respect to a defined set of criteria. The ICV concentration is at or near the calibration midpoint and is prepared from a different source than the calibration standards.

5.3.1 A synonym for ICV's is an Instrument Performance Check (IPC).

5.4 Continuing Calibration Verification (CCV) - A solution of the method analytes used to evaluate the performance of the instrument with respect to a defined set of criteria. The CCV concentration is varied throughout the calibration range.

5.5 Matrix Spike (MS) - An aliquot of a known sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed like a sample and its purpose is to determine whether the sample matrix contributes to the analytical results.

5.6 Field Duplicate (FD) - Two separate samples collected at the same time and placed under identical conditions and treated exactly the same way throughout the field and laboratory process.

5.7 Laboratory Control Sample (LCS) - An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether methodology is in control.

5.7.1 A synonym for LCS is a Lab Fortified Blank (LFB).

5.8 Linear Calibration Range (LCR) - The concentration range over which the instrument response is linear.

5.9 Method Blank - An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents and reagents which are used with other samples. The Method Blank is used to determine if method analytes or other interferences are present in the laboratory environment.

6.0 METHOD VARIATIONS

TATB is analyzed using a different instrument setup than that used for normal anions in accordance with SW846 9056 and EPA 300.0. These differences are described in sections 9.4.3, 9.5.3 and 11.4.

7.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

HYDROCHLORIC ACID IS A CORROSIVE AND A POISON.

SODIUM HYDROXIDE IS A CORROSIVE AND A POISON

TATB IS HIGHLY EXPLOSIVE AND SHOULD BE HANDLED WITH EXTREME CAUTION!

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

7.1 Wear eye protection with side shields while in the laboratory.

7.2 All chemicals and samples should be treated as a potential health hazard and exposure to these chemicals must be reduced to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). Individual sample MSDS forms provided by the clients are also maintained.

7.3 Personal protective equipment

7.3.1 Gloves are required when handling the chemicals in this procedure. The gloves approved for this procedure are:

7.3.1.1 Nitrile gloves for concentrated acids and bases.

7.3.1.2 Non sterile ambidextrous gloves for sample prep and standard handling.

7.3.2 Work under a hood when using concentrated acids and bases, and Acetonitrile.

7.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

7.4.1 Protect counter tops with counter paper or work from radioactive sample handling trays.

7.4.2 Prohibit admittance to immediate work area.

7.4.3 Post signs indicating radioactive samples are in the area.

7.4.4 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

7.4.5 Segregate radioactive wastes in radioactive waste containers are obtained from Waste Management.

7.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

7.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

7.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

7.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts.

7.7 In the event of an accident or medical emergency call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

7.8 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

8.0 INTERFERENCES/LIMITATIONS

8.1 Interferences may be caused by substances with similar retention times which overlap those of the anions of interest. High concentrations of one analyte may interfere with the detection of another analyte. Usually a sample dilution and/or a gradient elution will overcome interferences evidenced by retention time problems.

8.2 Limitations may occur if particulates remain in a sample after filtration, or if the client insists that the sample is analyzed without filtration.

8.3 Many interferences are caused by contaminants in the reagent water, reagents, glassware, etc., which lead to elevated baselines or artifacts on the chromatograms.

8.4 Any anion that is not retained by the column or just slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L this interference may not be significant.

8.5 Because nitrite, ortho-phosphate and bromide elute very closely together, they are potential interferants. When any of these anions are to be quantified in the presence of others dilutions may be necessary to completely resolve the analytes.

9.0 APPARATUS, MATERIALS, REAGENTS, EQUIPMENT AND INSTRUMENTATION

9.1 Apparatus and Equipment for Dionex IC:

9.1.1 Dionex 5 mL sample vials and filter caps or equivalent
9.1.2 Dionex 5 mL automated sampler cassettes or equivalent
9.1.3 4 L reservoirs
9.1.4 Helium tanks (minimum purity, 99.995%) or equivalent
9.1.5 1-5 mL Oxford, 10-100 µL, and 100-1000 µL Eppendorf pipets or equivalent
9.1.6 0.20 or 0.45 µm Acrodisc syringe filters or equivalent
9.1.7 10 cc disposable syringes or equivalent
9.1.8 100, 250 and 500 mL volumetric flasks
9.1.9 25, 50 and 100 mL graduated cylinders

9.2 Apparatus and Equipment for Metrohm Peak IC:

9.2.1 Metrohm 10ml sample vials and caps or equivalent
9.2.2 1L reservoirs: Working Eluent, 100mM H_2SO_4 and DI H_2O for suppressors.
9.2.3 Helium tank (minimum purity, 99.995%) or equivalent
9.2.4 1-5mL Oxford, 10-100µL and 100-1000 µL Eppendorf pipettes or equivalent.
9.2.5 0.20 or 0.45µm Acrodisc syringe filters or equivalent.
9.2.6 10cc disposable syringes or equivalent.
9.2.7 100, 250 and 500mL volumetric flasks
9.2.8 25, 50, and 100mL graduated cylinders.

9.3 Analyte Reagents: All reagents must be American Chemical Society certified or equivalent.

9.3.1 Potassium oxalate stock solution at 1000ppm
9.3.2 Sodium Chloride
9.3.3 NaOH
9.3.4 Acetonitrile
9.3.5 HCL (conc)
9.3.6 Sodium Carbonate
9.3.7 Sodium Bicarbonate
9.3.8 1,3,5-triaminotrinitrobenzene (TATB)- supplied by client
9.3.9 H_2SO_4 (conc)
9.3.10 Stock standards for anions of interest at concentration of 1000ppm or greater. These are usually purchased as certified solutions either in individual standards or in mixes of anions.
9.3.11 2-Fluorocinnamic Acid, 98% or equivalent (for use with Bomb Prep LCS))
9.3.12 Tin (IV) chloride bis (2,4-pentanedionate) (95% or equivalent) (for use in Bomb Prep LCS)
9.3.13 Adenine Sulfate 98% or equivalent (for use with Bomb Prep LCS)

9.3.14 2-Amino-5-Bromobenzoic acid 98% or equivalent (for use in Bomb Prep LCS)

9.4 Eluent for IC methods 9056/300.0 performed on the Dionex IC

9.4.1 Eluent stock: 12.0 mM sodium carbonate/8.0 mM sodium bicarbonate

Add 63.60g of sodium carbonate and 33.60g of sodium bicarbonate to a 1000mL volumetric flask and fill to volume.

9.4.2 Working eluent: Dilute 20mL stock (from 9.3.1) per liter of DI water

Sparge with Helium to degas.

9.4.3 Eluent for TATB: 0.152 M sodium carbonate/ 0.212 M sodium bicarbonate/ 0.171 sodium chloride solution.

Dissolve 20 g Na_2CO_3, 16.8 g $NaHCO_3$, and 10.0 g NaCL in approximately 800mL of DI H_2O. Stir until dissolved, then dilute to 1L.

Sparge with helium to degas.

9.5 Eluent for IC methods 9056/300.0 preformed on the Metrohm Peak IC.

9.5.1 Working Eluent: 3.2 mol/L sodium carbonate/1.0 mol/L sodium bicarbonate.

9.5.1.1 Add 0.339g of sodium carbonate and 0.084g of sodium bicarbonate to a 1000mL volumetric flask and fill to volume.

9.6 Column Cleaning Solution.

Combine 800mL acetonitrile with 20mLs conc HCL and 180mL DI.

9.7 Instrumentation:

9.7.1 Dionex Model 4500 Ion Chromatography instrument consisting of the following components:

9.7.1.1 Gradient pump Model GPM-2 or Model AGP-1

9.7.1.2 Autosampler Models ASM-3 and AS40

9.7.1.3 Conductivity Detector Model CDM-2 or CDM-3

9.7.1.4 Variable Wavelength Detector Model VDM-2

9.7.1.5 Eluent Degas Module Model EDM-2

9.7.1.6 Computer Interface: Advanced Computer Interface (ACI)

9.7.1.7 Computer: 486/33 PC of better

9.7.1.8 Instrument Operation Software: Dionex AI-450 V3.3.3.or equivalent

9.7.1.9 50 µL sample loop (used for anions methods)

9.7.1.10 1 mL sample loop (used for TATB)

9.7.2 Metrohm ion Chromatography instrument consisting of the following components:

9.7.2.1 709 IC Analytical Pump Module

9.7.2.2 788 Filtration Autosampler

9.7.2.3 732 IC Conductivity Detector with cell

9.7.2.4 IC separation Center with 2 injectors

9.7.2.5 Automation Interface, Dual Channel Full control \

9.7.2.6 IC Stand Alone Suppressor Module

9.7.2.7 Computer 486/33 PC or better

9.7.2.8 Instrument Operation Software: IC Net or equivalent

9.7.2.9 10mL sample loop (used for anions method)

9.7.3 Dionex columns for anions by 9056/300.0

9.7.3.1 Analytical Column; Dionex AS9HC

9.7.3.2 Guard Column; Dionex AG9HC

9.7.3.3 Precolumn: Hamilton PRP-1 cartridge

9.7.4 Metrohm Columns for Anions by 9056/300.0:

9.7.4.1 Analytical Columns: Metrostep A Supp 5

9.7.4.2 Guard Column: Metrohm RP Guard

9.7.5 Columns for TATB

9.7.5.1 Analytical Column: Dionex AS4ASC

9.7.5.2 Guard Column: Dionex AG4ASC

10.0 SAMPLE HANDLING AND PRESERVATION

10.1 Sample containers can be either glass or plastic. Samples should have no chemical additives for preservation purposes. All samples should be stored at an approximate temperature range of 4° ±2°C from the time of collection until the time of analysis.

10.2 All anions have 28-day holding times except nitrate (NO_3), nitrite (NO_2) and o-Phosphate - P (PO_4), which have 48 hours. There is no holding time stated for TATB. Holding times are calculated from the time and date of collection until the start of analysis, unless otherwise specified by the contract.

10.3 If sample analysis is not performed before holding time expires, the Project Manager will be notified. The project manager will determine if analysis should continue. If for any reason the project manger is unavailable, analysis will be performed and appropriate people notified as soon as possible.

10.4 Sample retrieval

10.4.1 The analyst/technician gives the list of samples needed to the sample custodian. The list is typically in the form of a computer-generated batch sheet and is placed on the clipboard outside of the main cooler. The sample custodian removes the appropriate samples from the cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

10.4.2 Analysts and technicians are responsible for retrieving their own samples on the weekends and after 5:00 p.m. on weekdays.

11.0 PREPARATION OF SAMPLES

11.1 All IC samples are marked in login as "UNPRESERVED"; only unpreserved samples should be run on the IC. Any sample preparation is done only with the consent of the analyst. Most sample preparations are in the form of filtrations and can be performed by using acrodisc filters and a syringe.

NOTE: It is assumed that material within the sample container is considered the "sample." Removal of any extraneous material (leaves, twigs, large rocks, etc.) must be documented in the case narrative.

11.2 Extractions: Most extractions are performed on soil samples where a known weight of approximately 4.0 g of sample is diluted with DI water to a volume of 40 mL. Mix thoroughly for a minimum of five minutes. The sample is then allowed to settle for a minimum of 30 minutes. After 30 minutes, if necessary, a centrifuge may be used. The extract is then filtered prior to injecting on the instrument. All prep data is recorded in ALPHA LIMS prep logbooks. TATB soil extractions are performed as above except 1ml of 5M NaOH is added to the sample. The vessel is allowed to heat at approximately 90°C in a water bath for approximately 1 hour prior to settling, centrifuging and filtering.

11.3 Bomb Prep: Bomb preps are performed on sample matrices such as coal or oil. Here a known weight of approximately 0.5 g of sample is used and after being bombed, the residuals are filtered into a 100 mL volumetric flask and brought to volume with DI water. For instructions on performing a bomb prep see GL-GC-E-079 for Bomb Preparation Method for Solid Waste. All material referenced from ASTM D 808-91. This prep procedure will not involve the various reagents from ASTM D 808-91 since the final analysis will be done by Ion Chromatography rather than gravimetrically. All prep data is recorded in the ALPHALIMS Prep logbook.

11.4 TATB liquid samples are spiked with 1mL of 5M NaOH solution to give optimal color development and to equilibrate the samples with the standard solutions.

12.0 PREPARATION OF STANDARDS SOLUTIONS AND QUALITY CONTROL STANDARDS

12.1 Vendor-prepared stock standards are used to prepare calibration and check standard solutions for this analysis. Both individual analyte solutions and mixes of analytes may be purchased for use as standards. All stock standards are at least 1000ppm concentration and are stable for at least one month when stored at 4 ± 2°C. Unopened stock solutions may be stored at ambient temperatures and their expiration is 1 yr from receipt or the manufacturer's expiration date, whichever is sooner. There must be at least 2 independent sources of standards materials for calibration and calibration verification standard preparation.

NOTE: Due to its extremely hazardous nature and limited availability, no second source sample is used for TATB analysis.

12.2 Calibration standards are prepared from stock standards at a minimum of five concentration levels per analyte. The working standards expire 24 hours after preparation.

12.3 Standard preparations are recorded in the ALPHA LIMS system for documentation and recording of standards and reagents. Refer to GC-LB-E-007 for details on assigning unique standard IDs and establishing traceability.

12.4 Laboratory control sample(s) (LCS) may be prepared from the calibration standard source.

12.5 Typical Calibration Standards preparations are as follows:

12.5.1 High Standards made from individual analyte parent standards

Analyte	Parent Conc	Parent V	Final V	Conc in Level 7
Fluoride	1000mg/L	1 ml	100ml	10 mg/L

Chloride	1000mg/L	2 ml	100ml	20 mg/L
Nitrite-N	1000mg/L	1 ml	100ml	10 mg/L
Bromide	1000mg/L	2 ml	100ml	20 mg/L
Nitrate-N	1000mg/L	1 ml	100ml	10 mg/L
o-Phosphate-P	1000mg/L	2 ml	100ml	20 mg/L
Sulfate	1000mg/L	4 ml	100ml	40 mg/L

12.5.2 High Standards made from Custom Mix (containing all analytes)

Analyte	Parent Conc.	Parent V	Final V	Conc. in Level 7
Fluoride	1000mg/L	1 ml	100ml	10 mg/L
Chloride	2000mg/L	1 ml	100ml	20 mg/L
Nitrite-N	1000mg/L	1 ml	100ml	10 mg/L
Bromide	2000mg/L	1 ml	100ml	20 mg/L
Nitrate-N	1000mg/L	1 ml	100ml	10 mg/L
o-Phosphate-P	2000mg/L	1 ml	100ml	20 mg/L
Sulfate	4000mg/L	1 ml	100ml	40 mg/L

12.5.3 Preparation of Calibration Standards, CCVs, ICVs and other standards

Cal Level	Parent	Parent V	Final V	Conc (of Fluoride)
Level 6	Level 7	50 ml	100 ml	5 mg/L
Level 5	Level 7	10 ml	100 ml	1 mg/L
Level 4	Level 7	5 ml	100 ml	0.5 mg/L
Level 3	Level 7	2.5 ml	100 ml	0.25 mg/L
Level 2	Level 7	1.0 ml	100 ml	0.10 mg/L
Level 1	DI	0.0 ml	100 ml	0.00 mg/L
High CCV	Level 7	75 ml	100 ml	7.5 mg/L

12.5.4 ICVs are prepared at Level 6 concentration but are a separate source from the standards used in the calibration curve.

12.5.5 CCVs are varied in concentration and may be from the same source as the calibration standards.

12.5.6 Spiking compounds are added from commercially prepared standards solutions such as is detailed here.

Analyte	Parent Conc	Parent V In Liquids	Parent V In Solids	Final V of aliquot	Final Conc
Fluoride	250 mg/L	100 ul		5 mls	5 mg/L
Fluorine	250 mg/L		800 ul	40 mls	5 mg/kg
Chloride	500 mg/L	100 ul		5 mls	10 mg/L
Chlorine	500 mg/L		800 ul	40 mls	10 mg/kg
Nitrite-N	250 mg/L	100 ul		5 mls	5 mg/L
Bromide	250 mg/L	100 ul		5 mls	5 mg/L
Bromine	250 mg/L		800 ul	40 mls	5 mg/kg
Nitrate-N	250 mg/L	100 ul		5 mls	5 mg/L
o-Phosph-P	500 mg/L	100 ul		5 mls	10 mg/L
Sulfate	1000mg/L	100 ul		5 mls	20 mg/L
Sulfur	334 mg/L		800 ul	40 mls	6.68 mg/kg

12.5.7 Preparation of Bomb Prep LCS Standard

Weigh 0.02g of each of the analytes listed in 9.3.11, 9.3.12, 9.3.13 and 9.3.14.

Add this amount into the bomb container and continue prep as for the other samples. Refer to 12.5.6 for true values.

13.0 INSTRUMENT CALIBRATION AND PERFORMANCE

13.1 Establish ion chromatographic operating conditions for the determination of target ions. An external calibration is then performed.

13.1.1 For each analyte of interest prepare a minimum of five calibration standards and a blank by adding accurately measured volumes of source standards to a known volume of reagent water. One of the calibration standards shall be at the PQL.

13.1.2 The standards are placed on the instrument (see Section 14.2) for analysis from highest to lowest. To automatically update the calibration curve enter AUTOCAL in the sample ID, followed by the level number.

13.1.3 Tabulate each concentration against area count. Include the blank in the linear calibration curve. Do not force the points through zero. The results determine a calibration curve.

13.1.4 The final calibration curve must have a correlation coefficient of .995 or better. If one standard is inconsistent with the rest of the standards it is acceptable to rerun that one standard and replace it in the curve.

13.1.5 If a sample analyte concentration is greater than the highest standard in the calibration range the sample will be diluted with reagent water to approximately mid range and reanalyzed.

13.1.6 The analytes retention time is updated from the last standard run. A typical retention window size is 5-10%. This can be modified based on the analyst's experience.

13.2 Calibration is verified daily or with every batch of samples. If the concentration or retention time window shifts by more than 10% from the expected value, a new calibration must be performed prior to the analysis of any samples.

13.3 Linear Calibration Range (LCR)- The LCR is determined initially by acceptance criteria of the curve of the curve (0.995 correlation coefficient or better for each analyte). It is verified by using a blank and at least 3 standards. The ICV which is run daily may be used as a LCR verification, and the alternating concentrations of CCVs may also be considered for the same purpose. Acceptance Criteria is 90-110% for all of these standards.

14.0 ANALYSIS AND INSTRUMENT OPERATION

14.1 Typical Run Sequence

14.1.1 ICV/IPC
14.1.2 ICB
14.1.3 MB (if required)
14.1.4 LCS (and LCS Duplicate if required)/LFB
14.1.5 Sample 1 through 8
14.1.6 Duplicate of any one sample
14.1.7 Spike of any one sample
14.1.6 Spike Duplicate of sample in 14.1.7 (if applicable)
14.1.8 CCV
14.1.9 CCB

14.1.10 One LCS (and LCS duplicate, if applicable) per batch of 20 samples, and one matrix duplicate, matrix spike, and matrix spike duplicate (if applicable) per batch of 10 or fewer samples.

NOTE: A CCV and CCB are to be run after every 10 samples and at the end of the analysis sequence.

14.2 Analysis by Dionex IC:

14.2.1 Fill the eluent reservoir as necessary with the proper eluent for the method that will be analyzed. This will be performed at the start of the working day. This will allow the daily checks to verify the calibration curve due to changing eluent.

14.2.2 Turn on the helium tank, if off, and adjust the regulator pressure to 100 psi. The tank should be left on at all times. When tank pressure reaches 100 psi change out the tank.

14.2.3 Locate the eluent degas module (EDM) and turn the "system" toggle switch to the "on" position, used reservoir to the "on" position, and the used reservoir's "mode" switch to the "sparge" position. The system pressure should be set to 5 to 10 psi.

14.2.4 Allow the eluent to sparge for at least five minutes.

14.2.5 Reduce the flow to just a small bubble rate in the eluent containers to conserve helium. Do not tighten the container caps. Keep the caps loose.

NOTE: The reservoir numbers directly correspond to the numbers located on the system's toggle switches.

14.2.6 All components except the Autosampler should be in the "remote" position.

14.2.7 Method: On the computer, call up the main menu on the AI-450 software. Select the "Method" function. A blank, untitled screen will appear. Most methods are generic and are simply renamed as necessary according to the IC file naming convention. Simply call up a previous method, rename it with the naming convention, making changes as necessary, save it in drive C, and use it as the new method. If a new method needs to be created, designate the parameters desired for the run. Such items include turning the pump, CDM, and VDM on or off as well as designating which eluent reservoir to use. Details of these and other features can be found in the Dionex AI-450 Chromatography Software User's Guide under "Method".

14.2.8 Schedule: It is good practice to create a new schedule daily. To do so call up main menu "Schedule"; at the blank schedule screen, enter the initial calibration and method verification sample names (ICV and ICB) and using the naming convention designate the data file names (EX: C:\TMP\HORIZON\AZHCDC input into the Horizon DataStore system.

14.2.9 Load: Go to the main menu "run" screen. At the run screen, choose "load". Under load, choose either "method" or "schedule" (if you have created a schedule in step 19.3, choose load schedule and the method from that schedule will also be loaded). Designate the method or schedule as demonstrated in step 19.3.

NOTE: For the CDM, the temperature compensation defaults to 1.7, and the output range is set to 10.0 µS. For the VDM, the output range is set at 0.1 AU and the wavelength must read 205 nm. With the carbonate/ bicarbonate eluent, the pump will

flow at 1.1 ml/min for anions, (1.0ml/min for TATB) and the pump pressure should normally be between 2200 and 2500 psi when using Dionex columns.

14.2.10 Prepare the initial rack of samples as follows:

14.2.10.1 In position #1, place a sample vial containing 5 mL of the ICV.
14.2.10.2 In position #2, place a sample vial containing 5 mL of the ICB.
14.2.10.3 Put caps on all of the vials and place this rack in the auto sampler with position #1 nearest the center.

14.2.11 Place 5 mL of the samples to be analyzed in the sample vials and place in the rack(s) as before; make necessary dilutions at this time.

14.2.12 With the first rack in the auto sampler, switch auto sampler "hold/run" switch to "run".

14.2.13 Go to the computer terminal and pull up the main menu "Run" screen.

14.2.14 On the run screen, under "load" choose "schedule."

NOTE: A method should have been loaded in the start-up procedure.

Sample, method, and datafile names are located in each schedule. Creating a schedule allows the analyst to designate which method to use for each sample in the run, as well as where and with what file name the analyst wishes to store the data. **Remember**, this run information should be entered in the main menu "Schedule" screen and saved with the appropriate naming convention.

NOTE: Section 22.1.11 is also described in the start up procedure.

14.2.15 At the load schedule screen, give the name of the schedule for the run. On the next screen, designate the injection number if other than 1 to start the run.

14.2.16 At this point (still under main menu run) make sure the auto sampler is in the run position and choose the "run" command.

14.2.17 Under run, select "start" and confirm at the OK prompt. The run will begin.

NOTE: Instrument shutdown is either performed manually or by method.

14.3 Manual Shutdown:

14.3.1 To perform a manual shutdown make sure all local/ remote switches are on local. Manual shutdown does not completely turn off the instrument but reduces flow to 0.5ml/min.

14.3.2 Proceed to turn off the system by first turning the pump off.

NOTE: For system #1, the self-regenerating suppressor (SRS) controller must be turned off prior to turning the pump off.

14.3.3 Finally, turn all the detector cells off.

14.4 Remote Shutdown:

14.4.1 To perform a remote method shutdown, make sure all local/remote switches, except the auto sampler (still on local), are on remote.

14.4.2 Go to the AI-450 main menu and choose the schedule icon. From there, each IC has its own shutdown method that can be reused day after day.

14.4.3 Under "file" select "open" and call up the active schedule.

14.4.4 In the method column, after the last sample, type the drive and the shutdown method name for the appropriate IC (found in C:\ as shtdwn1for

IC #1 or as shtdwn for IC #2). **Remember**, save any intentional changes made to the existing schedule.

14.5 New Shutdown Method:

14.5.1 If a new shutdown method is necessary, go to main menu method and designate in the method what items to turn off at shutdown and save the method.

14.5.2 Enter the method into the schedule the same as before. For further details see the AI-450 Software User's Guide.

14.6 Analysis by Metrohm Peak IC:

14.6.1 Fill the eluent reservoir as necessary with the proper eluent for the method that will be analyzed. This will be performed at the start of the working day. This will allow the daily checks to verify the calibration curve due to the changing eluent.

14.6.2 Turn on the helium tank, if off, and adjust the regulator pressure to 100 psi. The tank should be left on at all times. When tank pressure reaches 100 psi change out the tank.

14.6.3 All components should be on and the 709 IC pump Ext (remote) button ON.

14.6.4 Method:

On the computer, open the IC net software

Enter the Password (analyst specific)

Open the IC 4.smt system icon, open the control tab

Click on the Startup Hardware (Measure Baseline)

If the system is left on then Connect to Workplace remains checked.

14.6.5 Schedule:

Open the System tab

Click on the Sample Queue

Enter the new sample queue name, n815 (n=year, 8=month, 15=day)

Click on the edit button to enter the sample information/schedule.

After entering schedule, click on the green check button.

Open the report options icon, click on the printer and file options and enter the Sample Queue, i.e. n815, and click accept to close the window.

14.6.6 Load:

After the system has been on for about 15 minutes or until the baseline has become steady at zero, click Start on the Sample Queue window to start the schedule

NOTE: The flow is set for 0.7mL/min, the conductivity should be around 15uS, and the pump pressure should be between 4.5-4.9mPa when using the Metrohm column.

14.6.7 Prepare the initial samples as follows on the autosampler turret:

14.6.7.1 In position #1, place a sample vial containing 10mL of the ICV.

14.6.7.2 In position # 2 , place a sample vial containing 10mL of the ICB.

14.6.7.3 Place the remaining sample vials in order by the schedule.

14.6.7.4 Refill the tip and line rinse reservoirs with DI water.

14.7 Manual Shutdown:

14.7.1 In the IC net software, go to the IC 4.smt System icon, click Disconnect to Workplace. Close the IC Net software.

14.7.2 Turn off each component (turn the 762 IC interface off first).

14.8 Remote Shutdown:

14.8.1 All components remain on.

14.8.2 In the IC Net software, go to the IC 4.smt System icon, open the System tab, click on the Sample Queue, check the box Shut Down System after the Queue finishes. Do not close the IC Net Software.

15.0 EQUIPMENT AND INSTRUMENT MAINTENANCE

Routine maintenance for the IC most often includes the changing of eluent or of the helium tank, as well as, priming the pump and clearing the flow lines of any trapped air bubbles. It may also include any column work, such as cleaning, or it may call for regenerating the suppressor or changing of filters. These subjects are covered in the Dionex DX-300 Series Chromatography System manual and the Metrohm 8.110.1626 leaflet for Metrosep A Supp 5. The column cleaning solution is made as detailed in section 9.6.

16.0 DATA RECORDING, CALCULATION, AND REDUCTION METHODS

16.1 The raw data is processed by the IC software system. The software creates a data file including the method, which is stored on the network drive. The software then provides a print out with the following information: sample name, method used to process data, date and time run, (if report time differs from collection time both will be listed), analytes found with concentration, analytes not found and the sample chromatography.

16.2 An external program is used to generate a runlog, which is placed in the runlog binder. The runlog contains the following information in summary format: sample name, date and time run, batch number, dilution, QC type and description.

16.3 The following calculations are used in processing the data.

CSTD % Recovery = Reported Value/ Expected Value x100

RPD = Sample 1 - Sample 2/(Sample 1+ Sample 2)/2 x100

% Rec = Spike - Sample/Nominal Concentration x100

Bomb Prep = Sample x Final Volume/Sample Weight

Extraction = Sample x Final Volume/Sample Weight

16.3 For Bomb Calculation:

16.3.1 Calculate the concentrations of each element detected in the sample according to the following equation:

$$C_o = \frac{C_{com} \times V_{com} \times DF \times \%moisture \times 100}{W_o}$$

Where:

C_o = Concentration of element in the sample, mg/kg
C_{com} = Concentration of element in the combustate, mg/L
V_{com} = Total volume of combustate, mL
DF = Dilution Factor

W_o = Weight of sample combusted, g

16.4 A computer printout listing acceptable range for concentration and retention times will be generated. Each compound of interest will have to be within the acceptable range to be reported as a hit. If the instrument is re calibrated during the day, the retention windows will be reset after the multipoint is complete.

17.0 QUALITY CONTROL (QC) REQUIREMENTS

17.1 According to EPA Method 300.0, a formal Quality Control Program for this method must be maintained by each laboratory. The GEL QC Program for method 300.0 consists of 2 main components.

17.1.1 MDL Study: a new MDL study covering IC analytes under EPA 300.0 Part A is performed every 6 months, using the guidelines set forth in GL-LB-E-001.

17.1.2 Quality Control Sample (QCS) study: A commercially available standard (traceable to NIST standards when possible) is run each time a client, state, or federal performance evaluation study is done. The results of this known must be within the vendor guidelines for the PE sample result to be considered acceptable. If the result is not acceptable the analyst must troubleshoot the problem immediately and reanalyze both the vendor known and the PE sample.

18.0 INSTRUMENT AND BATCH QC REQUIREMENTS

18.1 Instrument QC

18.1.1 A calibration curve is run any time the values or retention times of the check standards shift by more than 10%.

18.1.2 An initial calibration verification (ICV) is run as the first sample in each day's run. When analyzing perchlorates, this is referred to as the Instrument Performance Check (IPC).

18.1.3 An initial calibration blank (ICB) is run following the ICV.

18.1.4 A continuing calibration verification (CCV) of varying concentration is run after every 10 analytical samples and after the last analytical samples in the run.

18.1.5 A continuing calibration blank (CCB) is run after every CCV.

18.1.6 The ICV, ICB, CCV's of varying concentrations, and CCB's are used throughout the analysis to constantly check the linear range of the instrument. The ICB and CCB must not exceed the concentration of the low standard in the calibration curve. The ICV and CCV's of the varying concentrations must recover within 10% of the true value of the standard.

18.2 Batch QC

18.2.1 A sample spike and sample duplicate are run for every batch of <10 samples and for each set of ten samples in batches with >10 samples.

18.2.2 A method blank and Laboratory Control Sample (LCS) are run at least once for every batch of 20 samples or less.

18.2.3 For solid batches where the sample is prepped using DI water extraction, the LCS is made by spiking the aliquot of the Source standard onto 40ml of DI water.

18.2.4 For nonaqueous liquids or solids not easily DI extracted, the LCS and method blank are bomb prepped in the same manner as the samples.

NOTE: Some clients have statements of work that call for additional QC such as LCS Duplicates or Matrix Spike Duplicates.

18.3 Acceptance limits:

18.3.1 Correlation coefficient must be 0.995 or greater.

18.3.2 ICV recovery must be 90-110% for all batches.

18.3.3 CCV recovery must be 90-110% recovery for all batches.

18.3.4 Matrix relative percent difference (RPD): is determined yearly by the Statistical Process Control (SPC) system of LIMS. The limits are given in spreadsheet form to each analyst.

18.3.5 Matrix spike recovery: The Limits are static at 80-120% recovery.

18.3.6 Method Blank: Must be less than the CRDL or Practical Quantition Limits (PQL).

18.3.7 LCS: is determined yearly by the Statistical Process Control (SPC) system of LIMS. The limits are given in spreadsheet form to each analyst. If the % Recovery falls outside these limits, the batch must be reanalyzed. For Method 300.0 the LCS acceptance limits are set at 90-110% for all liquid matrix batches.

18.3.8 LCS RPD: is determined yearly by the Statistical Process Control (SPC) system of LIMS. The limits are given in spreadsheet form to each analyst. If the RPD falls outside these limits, the batch must be reanalyzed.

19.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

19.1 Before submitting results for data entry into LIMS, check the following items:

19.1.1 The run is dated and initialed.

19.1.2 All cross-outs are dated and initialed.

19.1.3 Standard preparation is documented in the LIMS standards logbook and standard identification numbers are recorded with the run in LIMS.

19.1.4 All dilution factors are clearly marked.

19.1.5 Sample prep logbook in LIMS has been filled out completely.

19.1.6 Calculations are shown on the hard copy

19.1.6.1 Matrix and LCS duplicate RPDs
19.1.6.2 Matrix spikes and LCS recoveries
19.1.6.3 An example of the calculations used to obtain sample results

19.1.7 Correlation coefficient is recorded accurately and is $\geq$ 0.995.

19.1.8 All quality control samples such as blanks, duplicates, and spikes are clearly identified and fall within current acceptance limits.

19.1.9 The correct units are recorded for the results.

19.1.10 Each nonconformance has been noted in the comment section

19.1.11 All manual reprocessing of chromatograms must have a reason for the reprocess. The changes must be signed by the person doing the reprocessing and a qualified peer.

19.2 After ensuring that the above items are properly documented, print the batch report. (Data is automatically transferred to LIMS.)

19.3 Review data report to ensure that all data is in, then status the batch to "Review." This will trigger the qualifiers.

19.4 The batch sheet, data report, and case narrative are stapled together. This is the package that enters the main data review process.

19.5 The data review is done by the analyst who performed the analysis. The analyst completes the review, noting and correcting any discrepancies.

19.5.1 When the analyst has a correct report of the data, the package is passed on for peer review.

19.6 A qualified peer analyst then reviews the data package. He/she is responsible for checking all appropriate items on the data review checklist and documenting this review.

19.6.1 If typographical or transcription errors are found, the package is returned to the analyst for corrections. The peer is then responsible for verifying that the corrections have been made. The cycle of resubmitting the batch for data corrections and review continues until all errors have been corrected.

19.6.2 If the peer reviewer finds a discrepancy between the LIMS logbooks or the hard copy and the data report, it is his/her responsibility to address the matter with the analyst and to ensure that the appropriate corrections are made by the analyst, if possible.

19.6.3 If the batch does not meet the quality control requirements of the method, then the peer reviewer informs the team leader that the samples in that batch must be reanalyzed.

19.7 If the analyst is not available to review his/her data report, a second peer reviewer will be assigned by the team leader.

19.8 When the data package associated with a given batch satisfactorily passes review, the peer or analyst updates the batch to "DONE" status in LIMS.

19.9 The entire data package is stored for about six months. After six months, the data is removed and placed in the long-term storage facility.

20.0 RECORDS MANAGEMENT

All data associated with the activity described in this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

21.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

22.0 REFERENCES

22.1 Dionex DX-300 Series Chromatography System

22.2 Dionex AI-450 Chromatography Software User's Guide

22.3 Dionex Operational Techniques of Ion Chromatography Training Manual

22.4 Dionex AI-450 Training Manual

22.5 EPA Method 300.0, "The Determination of Inorganic Anions in Water by Ion Chromatography"

22.6 Standard Methods for the Examination of Water and Wastewater, Method 4110B, "Determination of Anions by Ion Chromatography", 18th edition.

22.7 SW 846, Method 9056, "Determination of Inorganic Anions by Ion Chromatography," September 1994.

22.8 Metrohm Metrodata IC Net 2.1

22.9 Metrohm 732 IC Detector/733 IC Separation Center Instructions for use 8.732.1033

22.10 Metrohm 709 IC Pump Instructions for use 8.709.1023

22.11 Metrohm 753 Suppressor Module Instructions for use 8.753.1003.

22.12 Metrohm 762 IC Interface Instructions for use 8.762.1003

22.13 Metrohm 688 IC Filtration Sample Processor Instructions for use 8.788.1003

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE FOR CYANIDE SAMPLE DISTILLATION

(GL-GC-E-067-REVISION 5)

APPLICABLE TO METHODS:
EPA Method 335.1, 335.3 and 335.4,
SW-846 Methods 9010B and 9012A,
and CLP Method 335.2-M.

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1.0 STANDARD OPERATING PROCEDURE FOR CYANIDE SAMPLE DISTILLATION

2.0 METHOD CODE

EPA Methods 335.1, 335.3 and 335.4, SW-846 Methods 9010B, 9012A, and CLP Method 335.2-M.

3.0 METHOD OBJECTIVE/PURPOSE

This standard operating procedure provides the necessary instructions for distilling samples of various matrices prior to analysis to determine the concentration of cyanide (CN) present.

GL-GC-E-095 is the analytical SOP.

4.0 METHOD SUMMARY

In this procedure, cyanide is released from cyanide complexes by acidification and heating. The cyanide in the form of hydrocyanic acid (HCN) is carried into a hydroxide scrubber solution. The cyanide in this solution is then determined by automated colorimetric means as detailed in GL-GC-E-095.

5.0 APPLICABLE MATRICES

5.1 Groundwater
5.2 Drinking water
5.3 Domestic and industrial wastewater
5.4 Soil
5.5 Sludge
5.6 Oil

NOTE: Clients may request that this analysis be performed on miscellaneous liquid, solid, air, or stack samples. In these cases the procedure is modified as necessary.

NOTE: DHEC requires SW-846 Method 9012 to be run for any matrices other than drinking and wastewater when data is to be used for regulatory purposes.

NOTE: As of October 1993, Method 335.4 has only been promulgated as a drinking water method.

6.0 HOLDING TIME

Holding time is 14 days from the time and date of collection until the start of analysis, unless otherwise specified by the contract.

NOTE: US EPA CLP requirements specify a holding time of 12 days following sample receipt by the contractor.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples should be stored in a 500 mL or larger plastic bottle.

7.2 Any liquid sample should be preserved with approximately 2 mL of 10 N sodium hydroxide per liter of sample.

7.3 The sample is stored at 4° C.

8.0 INTERFERENCES/LIMITATIONS

8.1 Possible sulfide interference is eliminated by the addition of bismuth nitrate as stated in SW-846 Method 9010A/9012 or by the addition of cadmium carbonate as stated in EPA Method 335.3.

8.2 Oxidizing agents that decompose cyanides may be removed by the addition of ascorbic acid or sodium arsenite. SW-846 Method 9010A recommends sodium arsenite, while 9012 and 335.3 recommend ascorbic acid. Sodium arsenite appears to yield more consistent results.

8.3 Thiocyanates produce a positive interference when they are decomposed to cyanide by ultraviolet digestion. This interference can be reduced by manual distillation.

8.4 Interferences from nitrates and nitrites are eliminated by using sulfamic acid.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 5 to 500 µg/L

9.2 Calibration range: 5 to 200 µg/L

9.3 Method detection limit (MDL): Updated annually (See current study).

9.4 Method precision: See current SPC (Statistical Process Control) limits for relative percent difference (RPD) found in the Lachat SPC log.

9.5 Method accuracy: See current SPC limits for % Spike Recovery found in the Lachat SPC log.

10.0 DEFINITIONS

Total Cyanide - Refers to all inorganic cyanides present, including those as soluble salts or metal complexes.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze client samples without supervision until they have been fully trained and have demonstrated the ability to generate acceptable data. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

12.1 Sample preparation data is recorded in the Distillation logbook.

12.2 When the sample prep is complete, the results are submitted for prep data entry into ALPHA LIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

SULFURIC ACID, ACETIC ACID, AND SODIUM HYDROXIDE ARE HIGHLY CORROSIVE

POTASSIUM CYANIDE IS A CORROSIVE AND A CHEMICAL ASPHYXIANT.

POTASSIUM CYANIDE EMITS TOXIC FUMES WHEN HEATED OR MIXED WITH AN ACID.

USE CAUTION WHEN HANDLING SODIUM ARSENITE IS A CARCINOGEN. AVOID INHALATION OR INGESTION.

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS

13.1 Wear eye protection with side shields while in the laboratory.

13.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the laboratory as well as a reference file of Material Safety Data Sheets (MSDS). Individual sample MSDS forms provided by the clients are also maintained.

13.3 Personal protective equipment

13.3.1 Gloves are required when handling the chemicals in this procedure. The gloves recommended for this procedure are:

13.3.1.1 Nitrile gloves for concentrated acids and bases, potassium cyanide, and sodium arsenite in neat form.

13.3.1.2 General purpose latex or vinyl gloves for sulfamic acid, bismuth nitrate, and magnesium chloride.

13.3.2 Work under a hood when using concentrated acids and bases.

13.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.4.1 Wear a plastic apron over lab coat when working with radioactive samples.

13.4.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

13.4.3 Prohibit admittance to immediate work area.

13.4.4 Post signs indicating radioactive samples are in the area.

13.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.4.6 Segregate radioactive wastes in the waste containers obtained from Waste Management.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers

13.6 Never leave gas cylinders unchained or untied, including when they are on the moving carts

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives a list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from the cooler and either delivers them to the analyst/technician or places them on the "pick-up" shelf in the main cooler.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Equipment

15.1.1 MIDI Cyanide Distillation System with all related glassware

15.1.2 Cold water source

15.1.3 Vacuum source

15.1.4 Well ventilated hood

15.1.5 Analytical balance capable of weighing to 2 decimal places

15.1.6 10-100 µL adjustable air displacement pipet

15.1.7 100-1000 µL adjustable air displacement pipet

15.1.8 1-5 mL adjustable pipet

15.1.9 Potassium iodide (KI) starch paper strips

15.2 Glassware

15.2.1 50 mL graduated cylinders

15.2.2 Various sizes of volumetric flasks for reagent preparation

15.2.3 *20* mL vials

16.0 REAGENTS

16.1 Raw materials:

16.1.1 ASTM Type II deionized (DI) water

16.1.2 Potassium cyanide, KCN (FW 56.11)

16.1.3 Sodium hydroxide, NaOH (FW 40.00)

16.1.4 Sulfamic acid, H_3NO_3S (FW 97.10)

16.1.5 Bismuth Nitrate Pentahydrate, $Bi(NO_3)\cdot 5H_2O$ (FW 485.07)

16.1.6 Magnesium chloride heptahydrate, $MgCl_2\cdot 6H_2O$

16.1.7 Glacial acetic acid, CH_3COOH

16.1.8 Dow Corning Antifoam 2210

16.1.9 Sodium arsenite, $NaAsO_2$

16.1.10 Sulfuric acid, H_2SO_4

16.2 Preparation of reagents:

16.2.1 Sodium hydroxide absorbing solution, 0.25 N

16.2.1.1 Weigh out 10 g NaOH pellets and place in a 1 L volumetric flask.

16.2.1.2 Dissolve and dilute to volume with DI water.

NOTE: This reagent may be prepared in larger quantities if the same proportions are used.

16.2.2 Bismuth nitrate solution, (0.124M)

16.2.2.1 Dissolve 60 g bismuth nitrate pentahydrate $Bi(NO_3)\cdot 5H_2O$ in 100 mL DI water.

16.2.2.2 While stirring, add 250 mL glacial acetic acid.

16.2.2.3 Pour solution into a 1000 mL volumetric flask and dilute to the mark with DI water.

16.2.3 Sulfamic acid solution, H_3NO_3S, (0.8N).

16.2.3.1 In a 1000 mL volumetric flask dissolve 80 g sulfamic acid.

16.2.3.2 Mix well and dilute to the mark with DI water.

16.2.4 Magnesium chloride solution

16.2.4.1 Weigh out 510 g $MgCl_2\cdot 6H_2O$

16.2.4.2 Add to a 1 L volumetric flask, dissolve, and dilute to volume with DI water.

16.2.5 Sodium arsenite solution (0.4 N)

CAUTION: Avoid skin contact. Wear gloves when preparing this solution.

16.2.5.1 In a 1000 mL volumetric flask dissolve 51.2 g sodium arsenite $NaAsO_2$ using DI water.

16.2.5.2 Bring up to volume with DI water and store in a Nalgene or glass container.

16.2.6 1:1 Sulfuric acid solution H_2SO_4

16.2.6.1 Pour 500 mL DI water into a 1000 mL graduated cylinder.

16.2.6.2 Under a hood, **carefully** add 500 mL concentrated sulfuric acid to the cylinder.

16.2.6.3 Wait at least 20 minutes for the solution to cool, then store in a 1L Nalgene or glass container.

WARNING:

This solution generates a tremendous amount of heat upon makeup.

16.2.7 Potassium Cyanide (KCN) solution, (1ml=1000ug CN-). Dissolve 2.51g of KCN and 2g KOH in 900ml of DI. Standardize with 0.0192N silver nitrate, $AgNO_3$. Dilute to appropriate concentration to achieve 1ml = 1000ug of CN-. Alternatively a certified standard may be purchased. Working standards as detailed in Appendix I are prepared from 100ug/L stock solution.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 18th Edition, (1992), Method 4500-CN D.

NOTE: All reagents are good for 6 months unless otherwise noted.

17.0 PREPARATION OF SAMPLES

17.1 Distillation of aqueous or homogenous solid samples using a Midi-Dist distillation unit (See Appendix I).

17.1.1 The unit should be assembled as described in Figure 1 of the MicroBlock Instruction Manual.

17.1.2 Using Potassium Iodide strips, test for presence of chlorine. If the paper turns blue after being placed in the sample, chlorine is present. Remove any chlorine by adding sodium arsenite solution dropwise until the KI starch paper shows no color change.

17.1.3 Using lead acetate paper, test for the presence of sulfides. If the paper turns black, sulfides are present. Add 2.5 mls of bismuth nitrate to the sample. Test the sample again with lead acetate paper. If sulfides are still present, add an adequate amount of bismuth nitrate to remove them.

17.1.4 Fill reflux tube with 50 mL liquid sample or a recorded weight of solid sample to which 50 mL of 0.25N NaOH solution is added.

NOTE: A sample weight of 1.0 g is normally used for solid samples

17.1.5 For method blanks use 50 mL of 0.25N NaOH solution.

17.1.6 For matrix spikes, pipet 50 uL of 100 mg/L stock standard solution into 50 mL of sample.

17.1.7 For liquid the LCS, pipet 25 uL of the second source 100 mg/L stock standard solution into 50 mL of 0.25N NaOH solution. This is the low, 50ug/L standard. For homogenous solid samples, weigh out 0.5g of solid CN stock standard to use as the LCS. The nominal concentration

on this purchased soil standard is approximately 277,000ug/kg. Diluting the distilled LCS by 50X prior to analysis yields approximately 55.4ug/kg, the low standard.

NOTE: Standards of a different concentration may require different dilution to approximate 50ug/kg results.

17.1.8 For ICVs pipet 75ul of the second source 100mg/L stock standard solution into 50mL of 0.25N NaOH solution. This is the high, 150ug/L standard. Both solid and liquid batches have the same ICV.

17.1.9 Add 50 mL 0.25 N NaOH solution to the absorber tube.

17.1.10 Assemble all glassware as described in Section 11 of the Setup section of the instruction manual.

17.1.11 Turn on the flow of cooling water to the reflux condensers. Adjust the flow of the water so that the flowmeter reads 6 GPH (gallons per hour)/sample. If all ten positions are used, the flow should be approximately 60 GPH.

17.1.12 Turn on the vacuum source stopcock.

17.1.13 Adjust each vacuum valve so that a rate of three bubbles per second is observed in each reflux tube.

17.1.14 Pipet 2.5 mL of sulfamic acid through each air inlet to eliminate interfaces from nitrates.

17.1.15 Pipet 5 mL of 1.1 sulfuric acid through the air inlet of each Reflux impinger.

17.1.16 Pipet 2 mL magnesium chloride solution though the air inlet.

17.1.17 Press the red rocker switch on the top of the instrument so that the red light glows

17.1.18 Set temperature to 150° C.

17.1.19 Set the timer for 1 hour. The heating block will automatically turn off. Allow approximately 15 minutes of cooling time before turning off cooling water and vacuum.

17.1.20 Close all vacuum control valves and disconnect each absorber gas inlet tube from the associated reflux impinger.

17.1.21 Starting on the right, open each vacuum valve to pull all solution out of the frit. Close each vacuum valve and remove each absorber impinger from the unit.

17.1.22 Each impinger may now be sealed with Parafilm or the contents of the impinger may be transferred to another type of sealed container. The distillate is then placed in a refrigerator at 4 C until time of analysis.

17.2 The analyst performing the distillations records the date, time, analyst initials, batch number, client, lab number, volume or weight of sample, and any necessary comments about the distillation into ALPHALIMS and prints a Prep Data Report to be maintained in the Distillation logbook.

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards is handled as described in GL-LB-E-007 for Laboratory Standards Documentation.

18.2 All standards are prepared according to the recipes found in Appendix II

18.3 Each Batch of samples must include the following pretreated and distilled QC items: Matrix Blank, (MB), Laboratory Control Standard (LCS), Matrix Spike (MS), Matrix Spike Duplicate (MSD) if requested by client, and Initial Calibration Verification (ICV).

18.4 Standards are prepared (in a 0.25N NaOH matrix) following the recipes in Appendix II

18.5 A method blank is run for every batch of samples.

18.6 An LCS is run at least once for every batch of 20 samples or less. An LCS duplicate is run only upon client request.

18.6.1 For liquid samples, the LCS is normally a 50 (low) µg/L standard taken through the same process as the samples.

18.6.2 For solid batches, the LCS is a solid standard from a standards supplier that is taken through the same process as the samples.

18.7 A matrix spike, and matrix duplicate are run for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples.

18.8 An initial calibration verification (ICV) is run immediately after the calibration curve. This standard must be made from a different source than the calibration standards and is normally prepared at 150 (high) ug/L. Both solid and liquid batches have the same ICV.

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

Refer to Section 17 of this method for details on startup of distillation apparatus.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

20.1 Batch QC

20.1.1 A method blank, matrix spike, and matrix duplicate are run for every batch of < 10 samples and for each set of ten samples in batches with > 10 samples.

20.1.2 An ICV (Initial Calibration Verification) standard is prepped with each batch. This is a 150 µg/L standard made up from the second source stock standard. Both Liquid and Solid Batches have the same ICV.

20.1.3 An LCS and (LCS duplicate if requested by the client) are run at least once for every batch of 20 samples or less.

20.1.4 The LCS is normally a 50 µg/L standard taken through the same process as the liquid samples.

20.1.5 For solid batches, the LCS is usually a solid standard from a standards supplier that is taken through the same process as the samples.

NOTE: For solid batches, a dilution of the LCS is required prior to instrument analysis.

21.0 RUN SEQUENCE

Refer to GL-GC-E-095 for Total Cyanide Analysis for the analytical run sequence.

22.0 PROCEDURE

This SOP is a prep method. For analytical methodology, refer to GL-GC-E-095 for Total Cyanide Analysis.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

Refer to section 17 for details of shutting the distillation apparatus down.

24.0 DATA REVIEW, VALIDATION, AND APPROVAL PROCEDURE

After distillation is complete, the prep batch data is entered into ALPHALIMS and the batch assigned DONE status. The analytical results are generated using GL-GC-E-095.

25.0 DATA TRANSMITTAL

When a batch is given General Chemistry departmental "DONE" status, the data becomes available to reporting personnel.

26.0 RECORDS MANAGEMENT

All data associated with the performance of this procedure, including relevant logbooks, are maintained as quality records in accordance with GL-QS-E-008 for the Management and Disposition of Quality Records.

27.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper disposal of sample and reagent wastes from this procedure, refer to the Laboratory Waste Management Plan, GL-LB-G-001.

28.0 METHOD VERIFICATION

28.1 The three different methods sometimes call for different reagents to remove interferences. For consistency, most of the reagents used in this SOP come from Method 9010A/9012. See Section 8 for more detailed explanations.

28.2 The concentrations of the bismuth nitrate and sulfamic acid solutions are doubled from the concentrations listed in Method 9010A/9012. This allows half the volume being added to the samples, avoiding dilution problems.

29.0 REFERENCES

29.1 Methods for Chemical Analysis of Water and Wastes. March 1984, EPA-600/4-79-020, "Cyanide", Method 335.3 (Colorimetric, Automated UV) Storet No. 00720, Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

29.2 EPA Method 335.4, "Determination of Total Cyanide by Semi-Automated Colorimetry," Revision 1.0, August 1993.

29.3 USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis, Document Number ILMO 3.0. "Method for Total Cyanide Analysis by Midi Distillation," Method 335.2 CLP-M (Semiautomated Spectrophotometric).

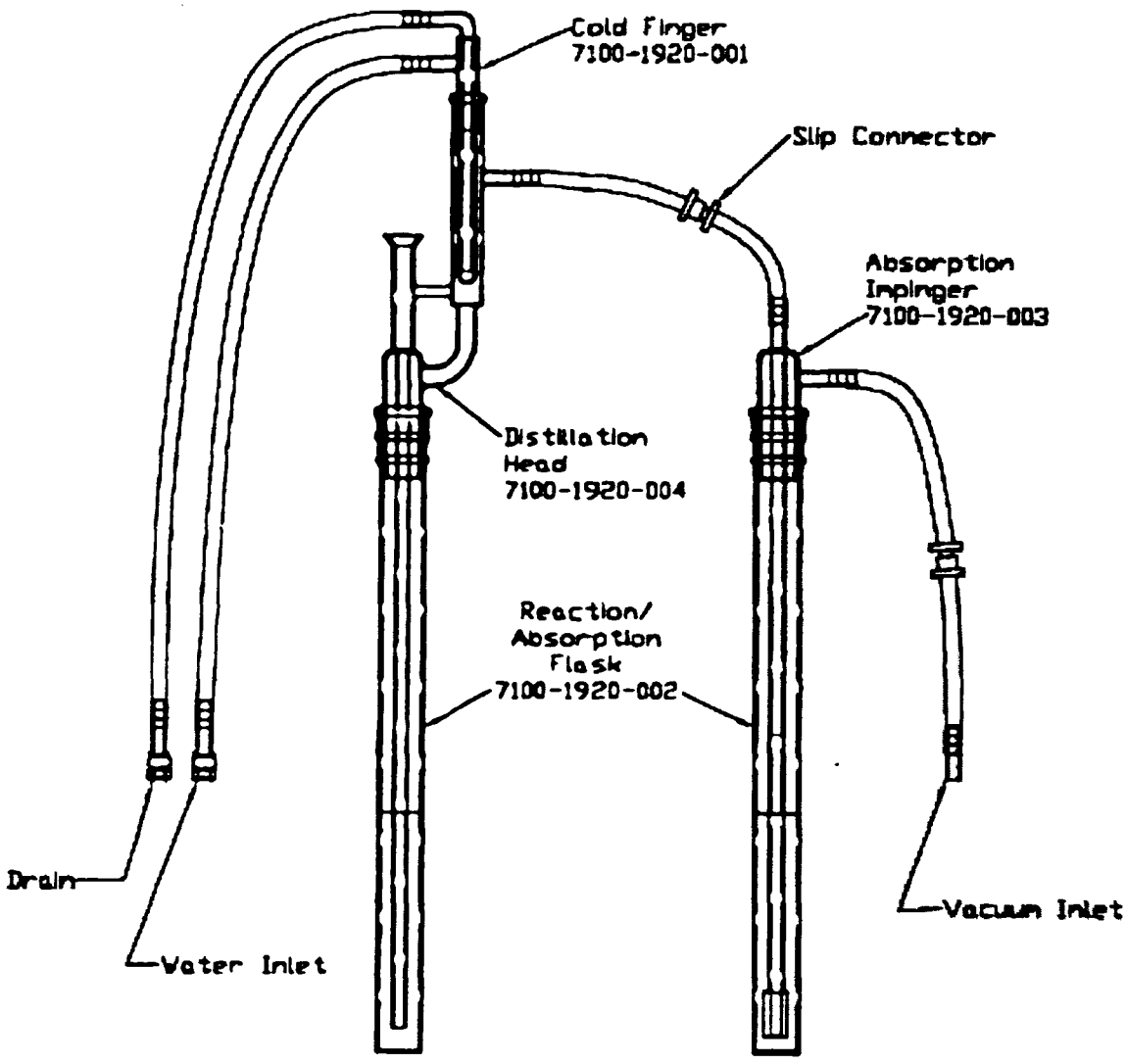
29.4 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume IC. SW-846, Third Edition, November 1986. Method 9012, "Total and Amenable Cyanide (Colorimetric, Automated UV)," Revision 0, September 1986. USEPA Office of Solid Waste and Emergency Response, Washington, D.C.

29.5 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume IC. SW-846, Third Edition, November 1986. Method 9010A, "Total and Amenable Cyanide (Colorimetric, Manual)," Revision 1, July 1992. USEPA Office of Solid Waste and Emergency Response, Washington, D.C.

APPENDIX I

Glassware Set-up

Figure 1



Cyanide Design A

APPENDIX II

Conc of Std	Init Vol of Stock	Final Vol of Std
200 ppb	200 µl of 100 ppm std	100 mL 0.25N NaOH
150 ppb	150 µl of 100 ppm std	100 mL 0.25N NaOH
100 ppb	100 µl of 100 ppm std	100 mL 0.25N NaOH
50 ppb	50 µl of 100 ppm std	100 mL 0.25N NaOH
10 ppb	10 µl of 100 ppm std	100 mL 0.25N NaOH
5 ppb	5 µl of 100 ppm std	100 mL 0.25N NaOH

WAD, Amenable, Total, Reactive, Free

VERIFY THE VALIDITY OF THIS SOP EACH DAY IN USE

STANDARD OPERATING PROCEDURE

FOR

CYANIDE ANALYSIS BY LACHAT QUIKCHEM 8000 FIA

(GL-GC-E-095 REVISION 2)

APPLICABLE TO METHODS:
EPA Methods 335.1, 335.3 and 335.4,
SW-846 Methods 9010B and 9012A,
And CLP Method 335.2-M

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1.0 STANDARD OPERATING PROCEDURE FOR TOTAL CYANIDE ANALYSIS BY LACHAT QUIKCHEM 8000 FIA

2.0 METHOD CODE

2.1 EPA Methods 335.1, 335.3 and 335.4

2.2 SW-846 Methods 9010B and 9012A

2.3 CLP Method 335.2-M

3.0 METHOD OBJECTIVE/PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to determine total cyanide in various sample matrices using the Lachat QuikChem 8000 Flow Injection Analyzer after the samples have been distilled by SOP GL-GC-E-067, and if necessary, pretreated for amenability to chlorination as in SOP GL-GC-E-040.

4.0 METHOD SUMMARY

Cyanide is released from cyanide complexes by digestion and distillation. The liberated hydrogen cyanide is converted to cyanogen chloride by reaction with chloramine-T reagent at a pH of less than eight. The cyanogen chloride then reacts with the pyridine-barbituric acid reagent to form a red colored complex. This complex is measured colorimetrically at 570 nm.

5.0 APPLICABLE MATRICES

5.1 Groundwater

5.2 Drinking water

5.3 Domestic and industrial wastewater

5.4 Soil

5.5 Sludge

5.6 Oil

NOTE: Clients may request that this analysis be performed on miscellaneous liquid, solid, air, or stack samples. In these cases the procedure is modified as necessary.

NOTE: CDHEC requires SW-846 Methods 9012A to be run for any matrices other than drinking and wastewater when data is to be used for regulatory purposes.

6.0 HOLDING TIME

Holding time is 14 days from the time and date of collection until sample preparation, unless otherwise specified by the contract.

NOTE: US EPA CLP requirements specify a holding time of <u>12 days following sample receipt</u> by the contractor.

7.0 SAMPLE CONTAINER/PRESERVATION/COLLECTION/STORAGE REQUIREMENTS

7.1 Samples should be stored in 500 mL or larger plastic or glass bottles.

7.2 Liquid samples are preserved with approximately 2 mL of 10 N sodium hydroxide per liter of sample to obtain a pH of 12 or higher.

7.3 The sample is refrigerated at 4°±2°C.

8.0 INTERFERENCES/LIMITATIONS

8.1 Possible sulfide interference is eliminated by the addition of bismuth nitrate as stated in SW-846 Methods 9010B and 9012A. This is added during distillation as detailed in SOP GL-GC-E-067.

8.2 Oxidizing agents that decompose cyanides may be removed by the addition of ascorbic acid or sodium arsenite. SW-846 Methods 9010B and 9012A recommend

sodium arsenite, while EPA 335.3 recommends ascorbic acid. Sodium Arsenite has produced consistent results and is added during distillation as detailed in SOP GL-GC-E-067.

8.3 Thiocyanates produce a positive interference when they are decomposed to cyanide by ultraviolet digestion. This interference can be reduced by manual distillation.

8.4 Interference from nitrates and nitrites is eliminated by using sulfamic acid. It is added during distillation as detailed in SOP GL-GC-E-067.

9.0 PERFORMANCE CHARACTERISTICS

9.1 Method concentration range: 5 to 500 µg/L (according to EPA Method 335.3)

9.2 Calibration range: 5 to 200 µg/L

9.3 Method detection limit (MDL): Updated yearly

9.4 CLP instrument detection limit (IDL): Updated quarterly

9.5 Method precision: See current Statistical Process Control (SPC) limits for relative percent difference (RPD)

9.6 Method accuracy: See current SPC limits for % Spike Recovery

10.0 DEFINITIONS

10.1 Total Cyanide - Refers to all inorganic cyanides present including those as soluble salts or metal complexes.

10.2 CRDL - Contract required detection limits.

11.0 ANALYST VERIFICATION

Technicians and analysts do not analyze samples without supervision until trained by qualified personnel and upon successful analysis of a proficiency sample. Training records are maintained as quality records.

12.0 DOCUMENTATION OF DATA

When Cyanide analysis is complete, the results are uploaded into ALPHA LIMS.

13.0 SAFETY PRECAUTIONS AND HAZARD WARNINGS

WARNING

SODIUM HYDROXIDE IS HIGHLY CORROSIVE.

HYDROCHLORIC ACID IS A CORROSIVE AND A POISON.

POTASSIUM CYANIDE IS A CORROSIVE AND A CHEMICAL ASPHYXIANT.

PREVENT SKIN AND EYE CONTACT BY USING SPECIFIED PERSONAL PROTECTIVE EQUIPMENT WHEN MAKING STOCK REAGENTS.

WORK UNDER A HOOD TO PREVENT INHALATION WHEN MAKING STOCK REAGENTS.

WARNING

POTASSIUM CYANIDE EMITS TOXIC FUMES WHEN HEATED OR MIXED WITH AN ACID. USE CAUTION WHEN HANDLING AND WEAR GLOVES.

WARNING

PYRIDINE IS FLAMMABLE AND A TOXIC UPON INHALATION. PREVENT INHALATION BY USING PYRIDINE UNDER A HOOD.

13.1 Wear eye protection with side shields while in the laboratory.

13.2 Treat all chemicals and samples as a potential health hazard and limit exposure to these chemicals to the lowest level possible. GEL maintains a current awareness file of OSHA regulations regarding the safe handling of the chemicals in the

laboratory. A reference file of Material Safety Data Sheets (MSDS) and individual sample MSDS forms are maintained in the laboratory.

13.3 Personal protective equipment

13.3.1 Gloves are required when handling the chemicals in this procedure. The gloves approved for this procedure are:

13.3.1.1 Nitrile gloves for concentrated acids and bases, and potassium cyanide in neat form.

13.3.1.2 Butyl gloves for Pyridine.

13.3.2 Work under a hood when using concentrated acids and bases, and Pyridine.

13.4 Prior to handling radioactive samples analysts must have had radiation safety training and understand their full responsibilities in radioactive sample handling. Some general guidelines follow:

13.4.1 Wear a plastic apron over lab coat when working with radioactive samples.

13.4.2 Protect counter tops with counter paper or work from radioactive sample handling trays.

13.4.3 Prohibit admittance to immediate work area.

13.4.4 Post signs indicating radioactive samples are in the area.

13.4.5 Take swipes of the counter tops upon completion of work. Deliver those swipes to the designated swipe count box.

13.4.6 Segregate radioactive wastes. Radioactive waste containers are obtained from Waste Management.

13.5 All samples, chemicals, extracts, and extraction residues must be transferred, delivered, and disposed of safely according to all related SOPs.

13.5.1 Segregate solid wastes from liquid wastes in the satellite area containers.

13.5.2 Segregate oil wastes from water-soluble wastes in the satellite area containers.

13.6 In the event of an accident or medical emergency call for help immediately. When time and safety permit, an accident report form should be completed and turned in to the safety committee.

13.7 Fire escape routes are posted in the lab and all personnel should be familiar with them. In addition, fire safety equipment such as fire extinguishers is located in the lab. Training is available on the proper operation of this equipment.

14.0 SAMPLE RECEIPT FOR ANALYSIS

14.1 The analyst/technician gives the list of samples needed to the sample custodian. The sample custodian removes the appropriate samples from the cooler and scans them to ALPHA LIMS using a barcode scanner. The analyst then takes custody of the samples and scans the batch to the area where the samples will be prepped or analyzed.

14.2 Analysts and technicians are responsible for retrieving their own samples when the sample custodian is not available.

15.0 INSTRUMENTATION/EQUIPMENT/GLASSWARE

15.1 Instrumentation

15.1.1 Lachat QuikChem 8000 Flow Injection Analyzer including:

15.1.1.1 Model ASX-500 XYZ autosampler

15.1.1.2 Model RP-100 Multichannel peristaltic cartridge pump

15.1.1.3 Reaction unit or manifold

15.1.1.4 Colorimetric detector

15.1.1.5 Data System

15.1.1.6 DRD Autodilutor Module

15.2 Equipment

15.2.1 25 µL syringe

15.2.2 10-100 µL adjustable micropipette

15.2.3 100-1000 µL adjustable micropipette

15.2.4 10 mL disposable sample cups

15.2.5 pH strips

16.0 REAGENTS

16.1 Raw materials: (Chemicals used for standards should be of ACS grade or equivalent.)

16.1.1 Barbituric acid, $C_4H_4NO_3$ (FW 128.09)

16.1.2 Chloramine-T, $CH_3C_6H_4SO_2NNaCl{\cdot}3H_2O$ (FW 281.70)

16.1.3 ASTM Type II deionized (DI) water

16.1.4 Hydrochloric acid, concentrated HCl (FW 36.46)

16.1.5 Potassium dihydrogen phosphate, KH_2PO_4 (FW 136.09)

16.1.6 Pyridine, C_5H_5N (FW 79.10)

16.1.7 Sodium hydroxide, NaOH (FW 40.00)

16.1.8 Potassium cyanide, KCN (FW 56.11)

16.2 Preparation of reagents:

16.2.1 Carrier, 0.25 M Sodium Hydroxide

16.2.1.1 In a 1L plastic container dissolve 10.0 g NaOH in *1L* DI water.

16.2.2 Phosphate Buffer, 0.71 M

16.2.2.1 In a 1L volumetric flask dissolve 97g potassium phosphate, monobasic, anhydrous, (KH_2PO_4) in approximately 800mL DI water.

16.2.2.2 Dilute to just below the mark with DI water and invert to mix. Stir for 30 minutes to dissolve completely. Prepare fresh monthly.

16.2.3 Chloramine-T

16.2.3.1 In a 500 mL volumetric flask dissolve 2.0 g chloramine-T in approximately 200 mL DI water.

16.2.3.2 Dilute to mark with DI water and mix well.

16.2.3.3 This reagent must be prepared daily.

16.2.4 Pyridine-Barbituric Acid Reagent

16.2.4.1 Working under a hood, place 15.0 g barbituric acid into a 1 L beaker. Use approximately 100 mL DI water to rinse the sides of the beaker.

16.2.4.2 Place the beaker on a stirring plate and insert a magnetic stirring bar.

16.2.4.3 While the solution is stirring, add 75.0mL pyridine and 15.0 mL hydrochloric acid.

16.2.4.4 Add 600 mL more DI water, cover the beaker, and continue stirring until the barbituric acid is completely dissolved.

16.2.4.5 Transfer the solution to a 1000 mL volumetric flask, dilute to the mark with DI water and mix well.

16.2.4.6 This solution must be prepared fresh weekly.

16.2.5 Potassium Cyanide (KCN) solution, (1ml=1000ug CN-).

16.2.5.1 Dissolve 2.51g of KCN and 2g KOH in 900ml of DI.

16.2.5.2 Standardize with 0.0192N silver nitrate, $AgNO_3$. Dilute to appropriate concentration to achieve 1ml = 1000ug of CN-.

16.2.5.3 Alternatively a certified standard may be purchased. Working standards as detailed in Appendix I are prepared from 100ug/L stock solution.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 18th Edition, (1992), Method 4500-CN D.

NOTE: All reagents are good for 6 months unless otherwise noted.

17.0 PREPARATION OF SAMPLES

Refer to GEL SOP "Total Cyanide Sample Preparation" (GL-GC-E-067).

NOTE: It is assumed that material within the sample container is considered "the sample." Removal of any extraneous material (twigs, leaves, large rocks, etc.) must be documented in the case narrative and bench logbooks.

18.0 PREPARATION OF STANDARDS

18.1 Documentation of standards is handled as described in GL-LB-E-007 for Laboratory Standards Documentation."

18.2 All standards are prepared from traceable solutions according to the recipes found in Appendix 1.

18.3 All cyanide standards, blanks, and samples are prepared using 0.25N sodium hydroxide as diluent.

18.4 All cyanide calibration standards are prepared fresh daily.

18.5 Batches logged for Method CLP 335.2-M must include a calibration standard at the Contract Required Detection Limit (CRDL).

19.0 INSTRUMENT/EQUIPMENT START-UP PROCEDURE

19.1 System start-up procedure:

NOTE: Before applying power to the system, check all electrical and hydraulic connections.

19.1.1 Press the power switch "**ON**" to apply power to the system.

19.1.2 Set up manifold as shown in Appendix II

19.1.3 Connect all reagent tubes and the sample line to containers of freshly prepared deionized water. Turn on pump and allow DI water to pump through the system as the instrument warms up to temperature.

19.1.4 Set the temperature to 60°C and allow 15 minutes to warm up.

19.1.5 Once the heater reaches 60°C move the reagent tubes from the DI water and place them in the appropriate reagents. Allow the flow of reagents to stabilize for 2 minutes. The flow should be smooth and consistent.

19.1.6 Place samples and/or standards in the autosampler. Input the information required by the data system, such as concentrations, replicates and QC scheme.

19.1.7 Place autodiluter diluent line in 0.25 M NaOH diluent.

19.1.8 Calibrate the instrument by injecting the standards *and begin analysis*.

19.2 Software startup

19.2.1 Power up the computer, monitor, and printer.

19.2.2 Click on 'Omnion FIA' icon

19.2.3 Refer to Lachat Software User Manual.

20.0 QUALITY CONTROL (QC) REQUIREMENTS

NOTE: Refer to GEL Quality Assurance Plan (GL-QS-B-001) for appropriate action regarding unacceptable quality control parameters.

20.1 Instrument QC

20.1.1 The instrument calibration at the start of the run must contain six standards plus a calibration blank. A linear fit is primarily used, although a quadratic fit is acceptable, if documented.

20.1.2 An initial calibration verification (ICV) is run immediately after the calibration curve. This standard must be made from a different source than the calibration standards and is a distilled standard.

20.1.3 An initial calibration blank (ICB) is run following the ICV.

20.1.4 A continuing calibration verification (CCV) is run after every 10 analytical samples and after the last analytical sample in the run. CCV standards are not distilled.

20.1.5 A continuing calibration blank (CCB) is run after every CCV and after the final CCV.

20.1.6 All instrument standards and blanks are made up using 0.25 N sodium hydroxide as diluent.

20.2 Batch QC

20.2.1 A matrix spike, and matrix duplicate are run for every batch of ≤ 10 samples and for each set of ten samples in batches with > 10 samples. A method blank is run for every batch of samples.

20.2.2 An ICV (Initial Calibration Verification) standard is prepped with each batch. This is a 150 µg/L (high) standard made up from the second source stock standard.

20.2.3 An LCS is run at least once for every batch of 20 samples or less. An LCS duplicate is run only upon client request.

20.2.4 For liquid samples, the LCS is normally a 50 µg/L (low) standard taken through the same process as the samples.

20.2.5 For solid batches, the LCS is a solid standard from a standards supplier that is taken through the same process as the samples.

NOTE: For solids batches, a 150 µg/L liquid standard ICV is also prepped.

20.3 Acceptance limits:

20.3.1 The coefficient of determination (R^2) must be 0.995 or greater. If the calibration fails, the calibration curve must be reanalyzed. If it still fails, all calibration standards must be re-made and a new calibration conducted.

20.3.2 ICV recovery must be 85-115% for all batches logged for Methods CLP 335.2-M and SW846 9012A. ICV recovery must be 90-110% for Method EPA335.4. If the ICV fails, the calibration curve must be reanalyzed. If the ICV fails again, new standards must be re-made and a new calibration conducted.

20.3.3 CCV recovery must be 85-115% for all batches logged for Method CLP 335.2-M. CCV recovery must be 90-110% for Methods EPA 335.4 and SW846-9012A. If the CCV fails, all samples bracketed by the out of control CCV must be re-analyzed.

20.3.4 Matrix relative percent difference (RPD): See current acceptance limits in LACHAT SPC logbook. If the RPD falls outside these limits, the analyst must enter a text value comment into ALPHALIMS.

20.3.5 Matrix spike recovery: Refer to current acceptance limits in LACHAT SPC logbook. If the %Spike Recovery falls outside these limits, the analyst must enter a text value comment into ALPHALIMS.

NOTE: The matrix spike recovery for CLP batches must fall between 75-125%. If not, a post spike must be added to the distilled sample. This value must also be reported. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more.

20.3.6 Prep blank and/or calibration blanks: Must be less than the CRDL.

20.3.7 LCS RPD: Refer to current acceptance limits in LACHAT SPC logbook. If the RPD falls outside these limits, the batch must be reanalyzed.

20.3.8 Due to the scope of the test and method, peaks are verified visually. These peaks should have a steady rise and fall. Any peak that is sharp in nature with jagged edges must be reanalyzed for verification.

21.0 RUN SEQUENCE

21.1 Calibration Standards: 200, 150, 100, 50, 10, 5, and 0 µg/L

21.2 ICV

21.3 ICB

21.4 5 ug/L standard (CRDL)

21.5 Up to 10 analytical samples including LCS, Method Blank, and sample QC (refer to Section 20)

21.6 CCV

21.7 CCB

21.8 Repeat steps 21.5 – 21.7 for remaining samples in the run. End with CCV and CCB.

22.0 PROCEDURE

22.1 Create Sample Table:

22.1.1 Click on 'Open' and choose file to open.

22.1.2 Fill in the Sample table according to the Run Sequence 21.0.

22.1.3 Enter the sample ID and dilution factor.

22.1.4 Check to ensure the cup location is incremented correctly.

22.1.5 Load samples onto the autosampler as listed on the printed sample table.

22.2 Check to make sure all reagents and lines are pumping correctly.

22.3 Click on 'Start'.

23.0 INSTRUMENT/EQUIPMENT SHUT-DOWN PROCEDURE

23.1 Place the reagent lines in deionized water and allow DI water to pump through the system for 5 minutes.

23.2 Remove the reagent tubes from the DI water and allow air to pump through the system for 5 minutes, or until water no longer appears in the lines.

23.3 Turn off power, and release platen tension.

24.0 DATA REDUCTION, REVIEW, VALIDATION, AND APPROVAL PROCEDURE

24.1 Refer to GL-LB-E-005 and GL-GC-E-092 for data review and validation procedures.

24.2 Data Reduction

24.2.2 Linear regression is used for calibration. The analyst must not force the calibration line through the origin.

24.2.2.1 Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

Where:

y = instrument response
a = slope of line (also called the "coefficient of x")
x = concentration of the calibration standard
b = the intercept

24.2.2.2 The analyst should not force the line through the origin, but have the intercept calculated from the standard data points.

24.2.2.3 The regression calculation will generate a correlation coefficient (R^2) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, R^2 must be ≥ 0.995. The calculated intercept value needs to be evaluated before reporting sample results.

24.2.2.4 A positive value for the intercept indicates that there is some threshold instrument response that is the limiting factor in establishing linearity. A negative intercept value can be transformed into an x-intercept value that respresents a threshold concentration which is the limitation. If the intercept is positive, then, as a general rule, results where the instrument response is less than three time (3x) the intercept value may be unreliable. This will afford some protection against false positive results. If

the intercept is negative, results below the concentration of the lowest concentration calibration standard may be unreliable.

NOTE: For Navy clients, these adjustments to the quantitation limits will apply to all samples analyzed using the regression line.

24.2.2.5 In calculating the sample concentrations, the regression equation is rearranged to solve for the concentration (x) as shown below:

$$x = \frac{(y - b)}{a}$$

24.2.2.6 The curve must meet all criteria set forth in Section 20.0

24.3 Calculation

24.3.1 Report the values for the Total CN concentration and the Chlorinated CN concentration in the CN-Cl logbook.

24.3.2 Subtract the Chlorinated value from the Total value to get the CN Amenable to Chlorination concentration.

24.3.3 If the final value is less than "0", the Amenable to Chlorination concentration is reported as "0" with a text value comment to explain the result.

24.3.4 If the Total CN value is less than the PQL (5 µg/L), the Amenable to Chlorination result is reported as "0".

24.4 Data Upload

24.4.1 Click on "Run" tab in RunProperties window.

24.4.2 Check box that says "export as CSV file."

24.4.3 Click on "Format" and "Export Now."

24.4.4 Click on "Upload to ALPHA LIMS" from desktop screen.

25.0 DATA TRANSMITTAL

Refer to GL-LB-E-005 and GL-GC-E-092 for data review and validation procedures.

26.0 RECORDS MANAGEMENT

All logbooks and data generated as a result of this procedure are maintained as quality records in accordance with GL-QS-E-008 for Quality Records Management and Disposition.

27.0 ROUTINE INSTRUMENT/EQUIPMENT MAINTENANCE

Refer to the Lachat QuickChem 8000 Operation Manual.

28.0 LABORATORY WASTE HANDLING AND DISPOSAL

For the proper handling and disposal of sample and reagent wastes from this procedure see GL-LB-G-001, the Laboratory Waste Management Plan.

29.0 METHOD VERIFICATION

29.1 The three different methods sometimes call for different reagents to remove interferences. For consistency, most of the reagents used in this SOP come from Method 9010B. See Section 8 for more detailed explanations.

29.2 The pyridine/barbituric acid concentration comes from the Lachat method. This is one-fourth the concentration listed in Method 9012A.

29.3 The standard curve concentrations listed in Section 7.4.1 of Method 9012A are not representative of the needs of the environmental testing industry. The

industry standard is to have a PQL of either 5 µg/L or 10 µg/L. Therefore, the curve shows lower concentration values.

30.0 REFERENCES

30.1 Methods for Chemical Analysis of Water and Wastes. March 1984, EPA-600/4-79-020, "Cyanide," Method 335.3 (Colorimetric, Automated UV) Storet No. 00720, Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. EPA, Cincinnati, Ohio 45268.

30.2 EPA Method 335.4, "Determination of Total Cyanide by Semi-Automated Colorimetry, Revision 1.0, August 1993.

30.3 USEPA Contract Laboratory Program Statement of Work for Inorganics Analysis, Document Number ILMO 3.0. "Method for Total Cyanide Analysis by Midi Distillation," Method 335.2 CLP-M (Semiautomated Spectrophotometric).

30.4 Test Methods for Evaluating Solid Waste: Laboratory Manual Physical/ Chemical Methods, Volume IC. SW-846, Third Edition, June 1997. USEPA Office of Solid Waste and Emergency Response, Washington, D.C. 20460.

30.4.1 Method 9012A, "Total and Amenable Cyanide (Colorimetric, Automated UV)," Revision 1, December 1996

30.4.3 Method 9010B, "Total and Amenable Cyanide (Distillation)," Revision 2, December 1996.

30.5 Lachat QuickChem 8000 Operation Manual, August, 2000, Lachat Instruments, Milwaukee, WI 53218.

30.6 QuikChem Method 10-204-00-1-A, "Determination of Cyanide in Waters," Revision 08/28/00.

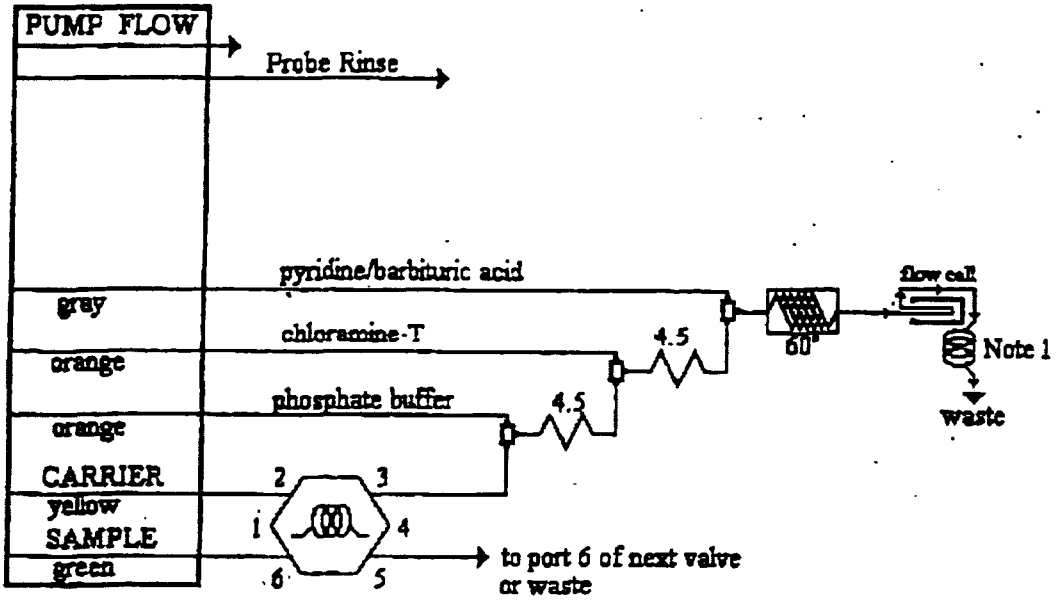
APPENDIX 1

Conc of STD	Vol of Stock	Final Vol of Std
200 ppb	200 µl of 100 ppm std	100 mL 0.25N NaOH
150 ppb	150 µl of 100 ppm std	100 mL 0.25N NaOH
100 ppb	100 µl of 100 ppm std	100 mL 0.25N NaOH
50 ppb	50 µl of 100 ppm std	100 mL 0.25N NaOH
10 ppb	10 µl of 100 ppm std	100 mL 0.25N NaOH
5 ppb	5 µl of 100 ppm std	100 mL 0.25N NaOH

WAD, Amenable, Total, Reactive, Free

APPENDIX 2

CYANIDE MANIFOLD DIAGRAM



Carrier: 0.25M sodium hydroxide solution (Reagent 1).
Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2 µL/cm.
AE Sample Loop: 150 cm x 0.8 mm i.d.
QC8000 Sample Loop: 150 cm x 0.8 mm i.d.
Interference Filter: 570 nm

Apparatus: An injection valve, a 10 mm path length flow cell , and a colorimetric detector module is required. The shows 650 cm of tubing wrapped around the heater block at the specified temperature.

4.5: 70 cm of tubing on a 4.5 cm coil support

Note 1: 200 cm backpressure loop, 0.52 mm i.d.

Section 1: Sample Receipt, Storage and Handling

Paradigm Analytical Laboratories - Standard Operating Procedure

Last Revised By:	Asst. Lab Director:	QA Officer:
W.M. Larkins	C.K. Cornwell	Greg Dickinson

Purpose

This SOP applies to all methods used in this lab and describes procedures used to record sample receipt and analysis information.

Summary

Samples arrive at PAL in the sample receiving area. The chain-of-custody and any other associated documentation is reviewed. Coolers are inspected for damage and then opened. Containers within the coolers are removed and inspected for damage. Temperature of each sample is measured using an infrared thermometer. If necessary, sample pH and proper use of any necessary preservatives are confirmed. Results of these inspections are noted on the Sample Receiving Checklist. Sample information is then entered into the LIMS system and samples are assigned unique identification codes. The LIMS system is then used to print a set of labels for each sample. These labels are used for the original containers received by the laboratory as well as glassware and containers used in the analytical procedures. The samples are stored in refrigerators and freezers, and temperatures in these units are monitored daily. Upon completion of the Sample Receipt process, the project folder is delivered to the Technical Director.

1.1 Login and Storage

1.1.1 Equipment

- Infrared thermometer

1.1.2 Supplies

- Folders, folder labels, and sample labels.

1.1.3 Procedure

- Upon delivery to the lab all containers will be checked for damage which may have affected the integrity of their contents.
- Containers, usually coolers, should be opened and contents examined for damage.
- Record the temperature as below in Section 1.2 on the chain-of-custody (COC). Sign and date/time the COC.
- Remove and examine contents. Verify that all information on the sample bottle labels match the COC. Fill out the Sample Receipt Checklist (SRC) and note any discrepancies.
- If air samples are present in the shipment, contact a member of management for a verification of sample identification.
- When required, check samples for correct preservation and pH.
- Enter sample information into the sample receipt log. The complete log consists of the LIMS information, the customers COC, the SRC. A printout of the LIMS information is stored in the project folder.

1.2 Temperature Measurement of Sample Containers

1.2.1 Equipment

- Infrared thermometer (IRT)

1.2.2 Procedure

1.2.2.1 Priority of temperature procedures

- Read the trip thermometer if present.
- Take temperature from temp blank (if present) using the IRT.
- Take temperature from a representative sample using the IRT.

1.2.2.2 Use of the IRT

- Turn on the unit and wait for a stable reading.
- If a sample is to be used for cooler temperature a 1L amber should be used. A 125mL plastic is the next choice. A 0.85 emmisitivity is used for both of these bottles. Be careful not to handle the bottle where you aim the gun. 40mL volatile containers may also be used with an emmisitivity of 0.86.
- The IRT is calibrated once per quarter.

1.3 Temperature Monitoring of Storage Units

1.3.1 Equipment/Supplies

- Walk-in cooler (Location W2)
- Freezer (Location F1)
- Logbook

1.3.2 Procedure

- All units contain thermometers that are traceable to NIST for accuracy.
- Each morning before heavy use of these units the temperature is recorded in the logbook.
- Refrigerators must be maintained at 4±2°C.
- Freezers must be kept at <-10°C. Thermostats are set at -20°C.

- Whenever these limits are not met, the failure is noted in the logbook. An attempt to correct the thermostat is made. A repeated failure warrants moving the samples to another unit and placing a service call to a vendor to repair the unit.

1.4 Sample Labeling

1.4.1 Summary

Sample labeling consists of applying water/organic solvent proof labels on the glass wall of the sample container (e.g., vials, centrifuge or other fraction-collection tube) and the bottle and bottle's cap for incoming samples. The labels must be durable and utilize indelible ink. The label contains information such as the Paradigm project/sample number and the clients sample identification. The PAL Project number is automatically generated by the LIMS system. All required sample containers will be pre-labeled at the start of any step.

1.4.2 Procedure

- Upon entry of the client's name into the LIMS, a new project number will be issued by the LIMS. This number is sequential and specific to the project (G100-1).
- Each individual sample container is assigned a unique laboratory sample identification number automatically by the LIMS (G100-1-3C)

1.4.3 Printing

Once the information is entered into the LIMS, a series of labels are printed which will be used to label the incoming sample bottle and cap. Additional labels will be printed at the time of sample extraction for use throughout the remainder of the laboratory processes. The labels must be waterproof and of appropriate size to accommodate the various sample containers. Additionally, the use of highlighted labels for QC samples such as the OPR is recommended

1.5 Sample Acceptance Policy

1.5.1 Summary

Samples received by the laboratory must meet certain criteria in order for the associated analytical data to meet method criteria. Samples must be properly documented and shipped in appropriate containers at specified temperatures. Holding times must be met and the amount of sample provided must be sufficient for the required extraction procedures.

1.5.2 Procedure

The validity and defensibility of analytical data is highly dependent upon proper delivery of samples to the laboratory. It may be impossible for the laboratory to perform the required analyses if samples are not properly documented and shipped in a timely fashion using appropriate containers and shipping materials. The following criteria are used to evaluate the suitability of samples prior to their acceptance for analysis:

a) Documentation: All samples must be accompanied by chain-of-custody forms indicating unique sample identification, date and time of sampling, location of collection, collector's name, any preservatives used, sample type (e.g., soil, water, etc.), requested analyses and any special remarks concerning the samples.

b) Chain-of-custody forms must accompany the samples and cannot be sent separately.

c) Sample Labeling: Each sample must be given a unique identifier that allows for cross-referencing with the chain-of-custody information. Sample labels must be durable enough to remain attached to the containers and utilize indelible ink to remain legible during shipping.

d) Sample Containers: Samples must be shipped in containers appropriate for the required analyses. Liquid and solid samples collected for organics analyses should be shipped in glass containers. Other matrices may require special containers (e.g., air samples). Any questions regarding sample containers must be resolved prior to collecting the samples. Containers should be packaged in such a way as to preclude breakage or leaking during shipping.

e) Damage: Samples should be inspected for signs of damage. *Discrepancy Procedure: Damaged containers must be safely repackaged and quarantined. Record the damage found and action taken. Report container damage to client services.*

f) Contamination: The shipment should be inspected for signs of contamination. Discrepancy Procedure: Safely separate the samples and remove any further means of contamination. Record the condition of the samples and action taken. Report potential contamination to client services.

g) Preservation: It is generally required that samples be chilled to < 4° C and kept at that temperature during shipping. Therefore, samples should be placed in insulated coolers with ice to keep them at or near this temperature until delivery at the laboratory. Samples that arrive above 6°C and are not on ice will be rejected and the client will be contacted for further instructions, such as re-sampling if for compliance monitoring. *Discrepancy Procedure: Inadequate preservation must be reported to client services.*

h) Holding Times: In order to provide accurate, defensible data, analytical methods strictly limit the amount of time that may elapse between collection and extraction of samples. Data taken from the analysis of samples which have exceeded the required holding times is generally considered to be invalid and is not legally defensible. Therefore, it is imperative that samples be sent to the laboratory as quickly as possible after collection. Ideally, the samples will be sent via overnight courier on the same day as collection. When this is not possible, the samples must arrive at the laboratory with enough time left to allow for proper login procedures before the holding time elapses. Samples received with few days left in the holding time may not be accepted by the laboratory.

i) Sample Volume: Sufficient sample volume must be sent for all required tests. Each method specifies the required sample volume for each applicable matrix. Questions regarding required sample volumes must be resolved prior to sampling.

j) Client Notification: When sample login is completed, a summary of the samples received and entered into the LIMS is generated. This can be faxed to the client upon request. This fax will include client sample ids, lab ids, dates, analyses requested and status summaries in short form.

The laboratory will attempt to contact the client and resolve any issues with sample acceptance. Samples that are immediately rejected are ones with improper preservation, damage, or show signs of contamination. In other cases, it may be possible to continue with analysis, although the analysis may be compromised. For instance, samples received with insufficient volume may be analyzed with the resulting data reflecting increased detection limits due to the insufficient volume, and minor discrepancies in sample documentation may be easily resolved. In such cases, the Technical Director/Project Manager will contact the client and describe the problem and any potential effects on the data. The client may then determine if the resulting data is likely to meet their needs. In other instances (e.g. samples received without labels or in broken containers), it may be impossible for the lab to proceed with analysis. In all cases, the Technical Director/Project Manager will make the final decision regarding the laboratory's acceptance of samples.

1.6 Internal Chain of Custody

- Samples requiring an Internal Chain of Custody (ICOC) as specified per client contracts will have ICOCs generated at the time of initial login. Each ICOC shall list the sample ID, number of containers received, and storage location as well as any pertinent information from the submitted COC. Login personnel will sign the ICOC and the samples, along with their respective ICOCs, will be released to a designated person from the extraction department. Samples requiring an ICOC are to be kept in locked storage to be accessed only by a designated person from the extraction department.
- After the sample has been extracted, the extraction department will generate a second ICOC to track the newly generated sample extract The ICOC for the extract will contain the same information as for the sample ICOC. All extracts will be kept in locked storage until the time of analysis. Only the designated person from the extraction lab and the GC/MS analyst shall have access to the controlled extract storage.

Section 4: 8290 Data Analysis & Reporting

Paradigm Analytical Labs - Standard Operating Procedure

Last Revised By:	Asst. Lab Director:	QA Officer:
W.M. Larkins	C K Cornwell	Greg Dickinson

Purpose

To describe the processes used in operating the HRGC/HRMS system, as well as the procedures followed in the generation, interpretation and review of laboratory data for Method 8290.

Summary

This SOP details how to analyze and report samples by EPA Method 8290 (Analyte list found in Table 1). HRGC/HRMS is used to detect and quantify PCDD/Fs Samples arrive at the MS lab having been extracted and fractionated using procedures in Section 3. Analyses are grouped into 12-hour runs, which include analyses of samples and standards mixtures. Upon completion of the run, the analyst reviews the data associated with both standards and samples in order to confirm the validity of the run and to determine any potential need for re-analysis or re-extraction. The analyst generates quantitation reports and chromatograms using sophisticated software These reports are used to generate forms that summarize the results of the analysis.

Table 1: Analyte List with Reporting Limits per Matrix

Analyte	Solid (pg/g)	Aqueous (pg/L)
2378-TCDD	1	10
12378-PeCDD	5	50
123478-HxCDD	5	50
123678-HxCDD	5	50
123789-HxCDD	5	50
1234678-HpCDD	5	50
OCDD	10	100
2378-TCDF	1	10
12378-PeCDF	5	50
23478-PeCDF	5	50
123478-HxCDF	5	50
123678-HxCDF	5	50
234678-HxCDF	5	50
123789-HxCDF	5	50
1234678-HpCDF	5	50
1234789-HpCDF	5	50
OCDF	10	100

4.1 Operation of HRGC/HRMS

4.1.1 Equipment

- HP6890 GC, Micromass Autospec Ultima high resolution mass spectrometer, vortex mixer, 10-100 uL pipette

4.1.2 Procedure

- Recall the GC temperature/pressure/flow program.
- Recall the MS experiment (see Table 2).
- Perform any necessary maintenance.
- Tune the MS resolution to 100 ppm at 5% height.
- Acquire location data to calibrate the MS and print a copy of function one MS resolution.
- Inject the window defining/GC resolution/continuing calibration mix (RETCON). Evaluate descriptor-switching times for accuracy. If any window defining peaks have shifted outside the descriptor windows, adjust the switching times before injecting any samples. This injection is also used to verify that there is less than or equal to 25% peak to valley for the two close eluters of 2,3,7,8-TCDD. Print a copy of the GC resolution check. If the valleys are within specifications, proceed to calibrate or verify a previous calibration. If not, further investigation and/or maintenance may be required. Re-inject this solution after maintenance to check for improvement.

- Now that the GC/MS resolution and descriptor switching times have been verified, a series of five initial calibration standards may be injected and reviewed for method requirements. If an initial calibration already exists, a RETCON may be analyzed to verify continuing calibration. If the curve or the RETCON passes method requirements, sample analysis may begin.
- Reconstitution of a sample is accomplished by adding nonane containing the injection standards (JS), capping the vial, and mixing well with a vortex mixer. The amount of standard to be added can be found in the spike profile document.
- Samples are injected under conditions identical to those used to establish calibration.
- A "back-end" RETCON must be injected within 12 H from the front end RETCON or the RETCON in the curve This standard is used to verify sufficient stability of the calibration after sample analysis. It has requirements set by the method. Depending on the back-end CS3 results, different calibration files maybe required to quantify the samples.
- A "back-end" print out of the MS resolution must also be performed.
- The calibration data from a sequence is filed in a folder cabinet under the day it was analyzed and includes the all GC/MS resolution checks, window verification, valley verification, front/back end RETCONs, runlogs and window defining mix (WDM) retention time sheets.
- Each sample hardcopy should include the quant report, totals pages, deviations, chromatograms, and report forms
- GC Column DB-5MS, 60 m, id 0.25 mm, 0.25 µm.

Table 2: Mass Descriptors used for Selected Ion Recording HRMS

Function (#)	Channel (#)	Mass (amu)	Dwell Time (ms)	I.C. Delay (ms)
1	1	303 9016	100	20
1	2	305 8987	100	10
1	3	315 9419	40	10
1	4	316 9824	20	10
1	5	316 9824	(Lock)	50
1	6	317 9389	40	10
1	7	319 8965	100	10
1	8	321 8936	100	10
1	9	327 8847	40	10
1	10	331 9368	40	10
1	11	333 9339	40	10
1	12	375 8364	30	20
2	1	339 8597	100	20
2	2	341 8568	100	10
2	3	351 9	40	10
2	4	353 897	40	10
2	5	355 8546	100	10
2	6	357 8517	100	10
2	7	366 9792	20	10
2	8	366 9792	(Lock)	50
2	9	367 8949	40	10
2	10	369 8919	40	10
2	11	409 7974	30	20
3	1	373 8207	100	20
3	2	375 8178	100	10
3	3	380 976	20	10
3	4	380 976	(Lock)	50
3	5	383.8639	40	10
3	6	385.861	40	10
3	7	389.8156	100	10
3	8	391.8127	100	10
3	9	401.8559	40	10
3	10	403.853	40	10
3	11	445.7555	30	20
4	1	407.7818	100	20
4	2	409.7788	100	10
4	3	417.8253	40	10
4	4	419.822	40	10
4	5	423.7767	100	10
4	6	425.7737	100	10
4	7	430.9728	20	10
4	8	430.9728	(Lock)	50
4	9	435.8169	40	10
4	10	437.814	40	10
4	11	479.7165	30	20
5	1	441.7427	100	20
5	2	443.7398	100	10
5	3	454.9728	20	10
5	4	454.9728	(Lock)	50
5	5	457.7377	100	10
5	6	459.7348	100	10
5	7	469.778	40	10
5	8	471.775	40	10
5	9	513.6775	30	20

4.2 Data Generation, Interpretation and Review

Paradigm Analytical Labs defines a batch of samples as no more than 20 samples processed with in a 12-hour shift. One LMB and one OPR are processed in every analytical batch, following the same procedures used for the field samples Generally, soil is replaced by salt (Na_2SO_4), effluent by deionized water and biological tissues by vegetable oil An invalid LMB or OPR requires a re-extraction of the affected samples.

4.2.1 Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. The use of high purity reagents and solvents helps minimize interference problems. All new materials used in the analysis shall be demonstrated to be free from interferences by running an initial reagent blank. Interferences co-extracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the analytes. The elimination of interferences is essential. Cleanup steps are used to reduce or eliminate these interferences and thereby permit reliable determination of the analyte as close as possible to the specified sensitivity.

4.2.2 Method Detection Limit Study and IPR Schedule

On an annual schedule, the laboratory shall perform a Method Detection Limit study (MDLs) utilizing a solid and aqueous matrix. MDLs are to be calculated for each 2,3,7,8-substituted congener. All MDL studies will be conducted following the guidelines set forth in 40 CFR, Part 136, appendix B. An MDL verification sample will be analyzed concurrently at an estimated 2 to 3 times the expected calculated MDL value for use with USACE clients. In addition, at the time of the MDL a continuing calibration will be analyzed at a concentration other than the normally utilized CS3 to further demonstrate instrument performance.

Each analyst is required to successfully complete an Initial Demonstration of Precision and Accuracy (IPR) before working on samples. An IPR is conducted for each matrix and extraction technique utilized. IPRs are repeated with each relevant change to a technique.

4.2.3 Initial Calibrations

On an annual schedule, Paradigm uses the concentrations in Table 4 to construct the initial calibration. The percent relative standard deviations for the mean response factors from the seventeen unlabeled standards must not exceed +/- 20%. The percent relative standard deviations from the labeled standards (i. e. extraction standards, cleanup standards and sampling standards) must not exceed +/- 30%. The signal to noise ratio for all signals present must be ≥ 10. The ion abundance ratios must be within specified control limits (see Table 3) Paradigm uses the concentrations in Table 4 to construct the initial calibration. The concentration of the lowest calibration point is a modification of the referenced method. It is lower than required.

Table 3. Theoretical Ion Abundance Ratios and Their Control Limits

Level of Chlorination	Theoretical Ratio	Control Limits	
		Lower	Upper
4	0.77	0.65	0.89
5	1.55	1.32	1.78
6	1.24	1.05	1.43
6[a]	0.51	0.43	0.59
7	1.04	0.88	1.20
7[b]	0.44	0.37	0.51
8	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF
[b] Used only for ^{13}C-HpCDF

A new initial calibration is required when the continuing calibration criteria below are not met. Routine maintenance may be performed to correct any failures. Any major maintenance to the analytical system such as slit cleaning, analyzer lens cleaning, magnet shifts, and detector disk changes warrant a new ICAL. At a minimum, a new initial calibration must be performed annually.

Table 4. Initial Calibration Concentrations

Analyte	CS-1	CS-2	CS-3	CS-4	CS-5
	Concentration (pg/µL)				
Unlabeled					
2378-TCDD	0.25	2	10	40	200
2378-TCDF	0.25	2	10	40	200
12378-PeCDD	1.25	10	50	200	1000
12378-PeCDF	1.25	10	50	200	1000
23478-PeCDF	1.25	10	50	200	1000
123478-HxCDD	1.25	10	50	200	1000
123678-HxCDD	1.25	10	50	200	1000
123789-HxCDD	1.25	10	50	200	1000
123478-HxCDF	1.25	10	50	200	1000
123678-HxCDF	1.25	10	50	200	1000
123789-HxCDF	1.25	10	50	200	1000
234678-HxCDF	1.25	10	50	200	1000
1234678-HpCDD	1.25	10	50	200	1000
1234678-HpCDF	1.25	10	50	200	1000
1234789-HpCDF	1.25	10	50	200	1000
OCDD	2.5	20	100	400	2000
OCDF	2.5	20	100	400	2000
Extraction Standards					
^{13}C-2378-TCDD	100	100	100	100	100
^{13}C-2378-TCDF	100	100	100	100	100
^{13}C-12378-PeCDD	100	100	100	100	100
^{13}C-12378-PeCDF	100	100	100	100	100
^{13}C-123678-HxCDD	100	100	100	100	100
^{13}C-123478-HxCDF	100	100	100	100	100
^{13}C-1234678-HpCDD	100	100	100	100	100
^{13}C-1234678-HpCDF	100	100	100	100	100
^{13}C-OCDD	200	200	200	200	200
Cleanup Standards					
^{37}Cl-2378-TCDD	0.25	2	10	40	200
^{13}C-23478-PeCDF	100	100	100	100	100
^{13}C-123478-HxCDD	100	100	100	100	100
^{13}C-123478-HxCDF	100	100	100	100	100
^{13}C-1234789-HpCDF	100	100	100	100	100
Injection Standards					
^{13}C-1234-TCDD	100	100	100	100	100
^{13}C-123789-HxCDD	100	100	100	100	100

4.2.4 Continuing Calibrations

Check that all paperwork is present. A CCal package should contain the documentation listed below.

- Pass: Run log. HRMS Resolution Checks. WDM retention time sheet. WDM chromatograms. GC performance for 2,3,7,8-TCDD. CCal quantitation page. CCal chromatograms. Injection preparation log
- Fail: The analyst listed on the run log can provide any missing paperwork.

Review the Run log.

- Pass: Check that the 12-hour windows have not been exceeded between the front end and back end CCals.
- Fail: Re-analysis of samples.

Review the HRMS Resolution checks.

- Pass: Verify 100ppm width at 5% height for PFK mass 318 or higher. Compare the resolution check times to those on the run log to be sure they bracket each sequence.
- Fail: Should a back-end resolution check fail, an assessment should be made to determine any data quality impact.

Review the Window Defining Mix and GC Performance Documentation.

- Pass: Check that the sample numbers on the WDM sheets match those on the runlog. Check that the retention times are correct for the WDM chromatograms.
- Check that the valley between 2,3,7,8-TCDD and its close eluters does not exceed 25%.
- Fail: Any missing peaks in the window-defining sample should be re-identified with a survey scan. Determine proper switching times. These must be entered into the HRMS ion function descriptors before analysis may resume. If the GC performance valley is greater than 25% instrument maintenance may be required. When a valley fails all samples must be reinjected.

Review the CCal Quantitation and Chromatograms.

- Pass: All ion ratios must be within the control limits given in Table 3. The measured RRFs obtained during the front and back-end CCals must be within ±20% of the mean values established during the ICAL for unlabeled standards, and within ±30% of the mean values for labeled standards. Quantitate using the ICAL when no compounds above 20/30% on the back-end retcon. Quantitate using averaged CCALs when there are no more than two unrelated compounds above 20/30% but less than 25/35% on the back-end retcon. If an RRF is biased high, the CCal is acceptable for all samples in which the failed analyte is not detected
- Fail: Routine instrument maintenance such as installing new injection port hardware, inner source cleaning, retuning, column clipping etc. will usually correct a calibration failure. If these measures do not work, then the laboratory will demonstrate performance after corrective action with either two consecutive acceptable CCALs or a new initial calibration.

Review the Injection Prep log sheet.

- Pass: Check that all samples have been spiked with 2 ng injection standard. Verify that final volume is 20 uL. Be sure that any dilutions or other comments are noted
- Fail: Calculations of sample concentrations should reflect any deviations from normal injection prep parameters.

4.2.5 Quality Control Work Groups

The following elements should be present in a complete work group file:

- LMB topsheets
- LMB totals sheets
- LMB chromatograms (11 pages)
- OPR topsheets
- OPR chromatograms
- Extraction log sheet
- Cleanup log sheet
- ASE/Cleanup observation forms
- Dry weight sheet (where applicable)
- Any additional information (ex. re-extract request sheet)

The following procedure should be used for reviewing a work group:

- Review the header information on the LMB topsheets. Verify that the method and client sample ID (LMB or OPR) are correct.
- Review the footer information on the LMB and OPR topsheets. Verify that the following information is correct: extraction date, analysis date, method, matrix, sample weight/volume, percent solids/lipids, pH, work group number, sample data file, retcheck data file, beginning cal data file, ending cal data file and ical data file.
- Verify that no target analytes are present in the LMB above the lower method calibration limit (LMCL). Verify that no target analytes are present above one-half the LMCL for USACE projects. And, that no estimated detection limits (EDL) exceed the LMCL. If target analytes or EDL's are above this limit, the associated samples must have concentrations that exceed 10 times the LMB concentration for the specified analyte. Otherwise, samples must be re-extracted.
- Review the totals data for the LMB. Be sure that any ghosting peaks are removed from the totals concentrations and the associated detection limits are elevated to reflect the subtracted peaks.
- Verify that extraction standards are within method specifications (40-135%) for the LMB and OPR, found on the topsheets.
- Verify that unlabeled recoveries in the OPR meet Paradigm's recovery limits of 70-130%.

4.2.6 Data Review

For quick reference, refer to the chart below

4.2.6.1 Initial Review

- Summary form generation and organization of Ical, Ccal, Samples and QC data is conducted by the analyst.
- Analysts review data upon generation and elicit peer review.
- Data is then released to a secondary review level with the analyst's signature.

4.2.6.2 Final Review

- Assemble project samples and QC data
- Review client information and documentation.
- Complete Data Review Checklist (Section 4, Appendix A) and sign reports.
- Samples are released to clients with the data reviewer's signature after the complete package is reviewed by a QA Manager or Lab Director.

Paradigm's Quality Control Requirements for Method 8290			
QC Check	**Frequency**	**Limits**	**Corrective Action**
Method Blank	One per extraction batch.	PCDD/F< SOP RL or <10% of level in sample.	Affected samples must be re-extracted.
Initial Calibration (ICAL)	As needed to maintain acceptable CCAL, after major maintenance, or at a minimum one per year	20% RPD for native and 30% RPD for labeled species.	An acceptable ICAL must be established before sample reporting may begin.
Mass Resolution	Before and after each 12 hour analytical sequence.	Mass resolution must be at 10,000 as estimated from a printout of a PFK peak.	MS maintenance.
Descriptor Defining Isomers	At the beginning of each 12h analytical sequence	First and last eluters must be present within the switching times..	Perform a survey scan to identify the correct switching times.
GC Performance Isomers	At the beginning of each 12h analytical sequence	Must be <25% valley.	GC maintenance.
OPR (LCS)	One per extraction batch	70-130 native.	Re-extract batch if low and detected. Evaluate data quality for high and non-detected.
OPRD (LCSD)	One per extraction batch	70-130. ≤ 20%RSD.	If needed and fails, re-extract batch.
Extraction Standards (ES)	Every sample must receive ES before extraction	40-135%.	Evaluate data quality, and if needed re-extract sample.
Continuing Calibration (CCAL)	Pre and post sample analysis within 12h	20/30%. Average CCALs if no more then 2 unrelated compounds above 20/30% but less than 25/35% on the back end.	Acceptable bracketing CCALs must be established before sample reporting may begin.
Lab Sample Duplicate (DUP)	Per client request	<25%Difference.	Flag failures.
Matrix spike/duplicate (MS/MSD)	One pair per method, per matrix, per extraction technique, per 30 days, per 20 samples	±25% recovery, 20% RPD.	Flag failures, report OPRD.

4.2.7 Calculations

4.2.7.1 Relative Response Factor

- $RRF = \frac{(\text{Sum Ion Abun. of analyte})(\text{ES Amount})}{(\text{Sum Ion Abun. ES})(\text{Analyte Amount})}$

4.2.7.2 Percent Difference, as for CCal evaluation.

- $\%D = \frac{(\text{CCal RRF} - \text{ICal RRF})(100)}{\text{ICal RRF}}$

4.2.7.3 Target compound calculation

- PCDD/PCDF (ppt) = $\frac{\text{(Sum Ion Abun. of analyte)(ES Amount)}}{\text{(Sum Ion Abun. of Int. Std)(RRF from ICal)(Amt. of Sample)}}$

- EMPC (ppt) = $\frac{\text{(Sum Ion Abun. of analyte)(ES Amount)}}{\text{(Sum Ion Abun. of Int. Std)(RRF from ICal)(Amt. of Sample)}}$

- EDL = $\frac{\text{2.5 (Height of Noise)(Std. Amount)}}{\text{(Height of Noise from Int. STD.)(RF from ICal)(Amt. of Sample)}}$

The instrumentation software calculates the noise level. However, manual noise determination may be employed at the reviewer's discretion in order to more accurately report peaks of interest

4.2.7.4 Extraction Standard Recovery Calculation

- % Recovery = $\frac{\text{(Sum Ion Abun. of ES)(JS Amount)}}{\text{(Sum Ion Abun. of JS)(ES RRF from ICal)(ES Amount)}}$

The clean up standard recoveries are calculated as above, substituting the ion abundances from the individual clean up standard for the extraction standard.

4.2.8 Requests for Re-extraction

Post-analysis is an early place to discover the need for re-extraction, so it is important to review all supporting data This includes spike profiles, extraction logs, clean-up logs, injection prep logs, observation forms and the sample tracking forms in the folder. The project or work group folder may contain exceptions or changes to our routine spiking procedures.

One should also check the sample for problems relating to analysis These problems include response factors that may introduce quantitative errors, interference that could be diluted out (yellow extracts), or any interference that causes de tuning or chromatographic conditions that could lead to quantitative errors.

Many things can cause the need for a re-extraction Extraction or clean-up recovery problems not detailed in the related paperwork indicate the need to talk to the person(s) involved. This type of communication can solve difficult problems and help to ensure that the re-extraction is planned well.

In planning a re-extraction the involvement of a technical reviewer is invaluable. Reviewers notice trends and problems that may call the need for re extracting a batch of samples. They can give insights as to whether re-extraction will even help or if a different extraction approach should be considered.

Our QA/QC officer should be consulted when re-extraction is considered so that the impact on other samples, or potentially a batch can be accessed

The QA/QC officer will schedule the re-extraction(s) by generating a form indicating the information necessary for the lab to do the re-extraction Some info includes the sample id, re-extraction due date, and reason for re-extraction (ref form DC18)

When the GC/MS analyst receives the form, the samples are marked "REX" in the LIMS.

When the extractionist receives the form, the samples are scheduled in as other samples are; they can tell that this is a re extraction by the REX indicator in the report column. The sample id will receive an R suffix for the re-extraction If for any reason a sample requires a second or third re-extraction, the sample id suffix will change to S, then T, and so on The sample id with the suffix should be used in all paperwork (extraction, clean up, injection prep, and run logs)

4.3 Safety

4.3.1 Each employee must read, understand and follow the safety guidelines in the Chemical Hygiene Plan

4.3.2 For further safety precautions, please refer to the referenced test method.

4.4 References

Method 8290. Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS), Revision 0, September, 1994.

Controlled documents referenced for sample preparation include DC 01-12, 16-18, 24, 27-29 and 55.

Last Revised by Mike Larkins
Signature:

Approved by Greg Dickinson
Signature:

Section 4: Appendix A--Data Review Checklist

Paradigm Analytical Labs - Standard Operating Procedure

PAL Project No.:

No. Of Samples:

Method: 8290; 1613; 23

Data Review Check List

Work Group: _____ Pass ☐ Flag ☐
_____ ☐ ☐
_____ ☐ ☐

ConCal: _____ Pass ☐ Flag ☐
_____ ☐ ☐
_____ ☐ ☐

ICAL: m8290-122203b
m8290-b111003b
m1613-122203b
m1613- b111003b

Item	
1. Project Information	
➢ Check COC and any correspondence for special instructions.	
➢ Verify that COC is signed and dated.	
➢ Verify that method information is correct.	
➢ Login report is present.	
➢ Check SRC for anomalies.	
➢ Verify that number of samples is consistent with client's request and COC.	
➢ Verify sample collection and receipt dates on sample datasheets.	
➢ Mark folder if EDD is required.	
2. Work Group Review **(Scanned)**	
➢ Verify sample preparation information	
➢ Note any comments on the bench sheets.	
➢ Verify that any positive results in the LMB are less than the MCL or ML (1/2 ML for USACE)	
➢ Verify that OPR meets recovery requirements.	
➢ Check %solids table for transcription errors.	
➢ Verify sample extraction date, matrix, weight, and volume.	
➢ Check OPR/OPRD form for consistency.	
➢ If applicable, include raw data for batch QC sample, ms and msd and MS/MSD form.	
3. Instrument Performance Review **(Scanned)**	
➢ Injection log: verify the time and date for the system performance checks (12-hr)	
➢ 100 ppm in mass for the resolution at m/z 331.	
➢ <25% valley for 2,3,7,8-TCDD	
➢ RRFs in ConCal are within ±20% (unlabeled) and ±30% (labeled).	
➢ If back-end RRFs within ±25% (unlabeled) and ±35% (labeled), bracketing RRF's are averaged when no more than two unrelated cmpds are effected.	
➢ Verify that ion abundance ratios passed.	
➢ Label first and last eluters in window defining mix chromatography.	
➢ Verify sample filename, ICAL, and RetCon files on datasheets.	
➢ Compare instrument run log with the injection prep log to account for all sample/std. injections.	
4. Sample Data Review	
➢ Verify client name.	

➢ Verify project ID.	
➢ Verify method.	
➢ ES, SS, and CS meet method requirements.	
➢ Averaged RRFs are used for computation, if applicable.	
➢ Check for RT shift.	
➢ Check that DL is raised to allow for any ghosting of ES.	
➢ Check first eluting PeCDF.	
➢ Examine SICPs for saturated peaks; check that dilution is reported.	
➢ QC check ion does not vary by more than ± 20% within the RT windows (Q).	
➢ Examine PCDPE SICPs for the co-eluting interferences (DPE).	
➢ Verify s/n: all peaks within RT window >2.5 x s/n appear on datasheet as either positive or EMPC.	
➢ Perform manual calculation (using total ion response and prep raw data) of native analyte.	
➢ Perform manual calculation (using total ion response and prep raw data) of ES and CS recovery.	
➢ Check resolution of 2378-TCDF, if positive. Check 2348- integration, if present.	
➢ Verify that MCL is correct for "A" qualifier.	
➢ Detected congeners do not have ND for totals.	
➢ Correct units appear on datasheets.	
➢ EMPC for congener must have EMPC value for totals.	
➢ Verify that the correct TEF s have been reported.	
➢ Check totals calculation for at least one sample.	
➢ Check TEF calculation for at least one sample in a project.	
➢ Calculate EDL for at least one sample in a project	

Notes to be used for the Cover Letter or Narrative

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Method 8310

TITLE: Determination of PAH by HPLC		
Reviewer: S. Cieri		Peer Reviewer: T. Uebler
Implementation Date: 2/23/04		Last Review Date: 2/17/04
Revision: 7	Status: Final	Method: 8310

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedure for the HPLC analysis of PAH compounds from extracts of water or soil matrices.

1.2 Use of Method 8310 presupposes a high expectation of finding specific compounds of interest (Section 1.2, Method 8310). No HPLC column has been developed for the confirmation of all PAHs. Fluorescence detection provides a more sensitive detector for some compounds. It is not a means of confirmation.

1.3 For routine testing, all positive PAH results are flagged as "not confirmed with a second column." Additional information concerning a positive identification may be available from another analysis performed on the same sample (e.g., semivolatile analysis by GCMS). See Section 13 for project-specific requirements regarding second columns.

2.0 METHOD SUMMARY

2.1 A water sample is extracted with methylene chloride using separatory funnel or continuous liquid/liquid extractor techniques; soils are prepared using sonication.

2.2 Extracts are concentrated, and the methylene chloride exchanged to acetonitrile.

2.3 This final extract is analyzed on a reverse phase HPLC column with ultraviolet (UV) detection.

3.0 HEALTH AND SAFETY

3.1 Many of the target compounds are classified as carcinogens. Preparation of all standards should be performed in a laboratory hood with proper ventilation.

3.2 All laboratory employees should protect themselves at a minimum with protective gloves, lab coat, and safety glasses. For more information see the Analytical Services Center Chemical Hygiene Plan located in the QA Library Island, shelf 2.

3.3 **Pollution Prevention** – Purchase chemicals based on expected usage, shelf life, and disposal cost. Prepare standard volumes on anticipated usage. Make appropriately sized dilutions and use serial dilutions where practical.

4.0 REFERENCES

4.1 Method 8310, Rev. 0 (9/86), SW846, Third Edition, Update III, June 1997.

4.2 SOP EXT.13 (water) and SOP EXT.25 (solids).

4.3 Level 1 Initial and Level 2 Peer Data Review Checklist (C-037).

4.4 Training SOPs QA.5 and A.23.

4.5 Data Review SOP A.25.

4.6 Laboratory Quality Assurance Manual (L-001).

4.7 MDL SOP A.18.

4.8 Corrective Action Procedure SOP QA.1.

5.0 DEFINITIONS/ACRONYMS

5.1 See generic list in the Quality Assurance Manual.

6.0 INTERFERENCES/POTENTIAL PROBLEMS

6.1 Solvents, reagents, glassware may cause discrete artifacts and/or elevated baselines. All of these materials must be demonstrated to be free from interferences.

6.2 The chromatographic conditions described allow for a unique resolution of the specific PAH compounds. Other PAH compounds, in addition to matrix artifacts, may interfere.

7.0 INSTRUMENTATION AND EQUIPMENT

Equipment:

Filtering apparatus, 13-mm 0.2-µM PTFE
Gastight syringes (1-mL, 50-, 100-, and 500-µL)
Pasteur pipettes
2 mL Autosampler vial with Teflon®-lined cap

HPLC System:

Hewlett-Packard HP1050 HPLC equipped with an HP variable UV wavelength detector.
#79853A, fixed at 254 nm
HP quaternary pump #79852A
HP auto sampler #79855A – Equipped to deliver 25 µL injection volume
C-18 Reverse phase HPLC column, Keystone Hypersil 100 cm x 4.6 mm
C-18 Reverse phase HPLC column, Phenomenex Envirosep 125 cm x 3.2 mm
HP data system
HP column heater

8.0 REAGENTS AND MATERIALS

8.1 See Table 8-1, Summary of Standards, Reagents, and Consumables.

Table 8-1

SUMMARY OF STANDARDS AND REAGENTS

Description	Source	Compound	Concentration (µg/mL)
PAH Calibration Mix	Accustandard or equivalent	Acenaphthlene	500
		Acenaphthylene	500
		Anthracene	50
		Benzo(a)anthracene	50
		Benzo(a)pyrene	50
		Benzo(b)fluoranthene	100
		Benzo(ghi)perylene	250
		Benzo(k)fluoranthene	100
		Chrysene	250
		Dibenzo(a,h)anthracene	100
		Fluoranthene	500
		Fluorene	1000
		Indeno(1,2,3-cd)pyrene	100
		Naphthalene	500
		Phenanthrene	500
		Pyrene	500
1-Methylnaphthalene 2-Methylnaphthalene Mix	Accustandard or equivalent	1-methylnaphthalene	1000
		2-methylnaphthalene	1000
1-Methylnaphthalene 2-Methylnaphthalene Mix (2nd source)	Absolute Standards Inc.	1-methylnaphthalene	1000
		2-methylnaphthalene	1000
PAH Reference Mix (2nd source)	Ultra Scientific or equivalent	Acenaphthene	500
		Acenaphthylene	500
		Anthracene	50
		Benzo(a)anthracene	50
		Benzo(a)pyrene	100
		Benzo(b)fluoranthene	100
		Benzo(k)fluoranthene	100
		Benzo(g,h,i)perylene	250

Table 8-1

SUMMARY OF STANDARDS AND REAGENTS

Description	Source	Compound	Concentration (µg/mL)
		Chrysene	250
		Dibenzo(a,h)anthracene	100
		Fluoranthene	500
		Fluorene	1000
		Indeno(1,2,3-cd)pyrene	100
		Naphthalene	500
		Phenanthrene	500
		Pyrene	500
ASTM Type II water	ASC water purification system	ASTM Type II water	NA
Methylene chloride Ultra Resi grade	J.T. Baker or equivalent	Methylene chloride	Neat
Acetonitrile – HPLC grade	J.T. Baker or equivalent	Acetonitrile	Neat
Surrogate, Terphenyl-d_{14}	Cambridge Isotope Labs	Terphenyl-d_{14}	Neat
Decafluorobiphenyl (DFB) Stock (2nd surrogate)	Ultra Scientific or equivalent	Decafluorobiphenyl	1000

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8.2 Stock standards expire 1 year from the date opened, unless an earlier vendor-supplied expiration date supercedes. Intermediate standards are good for 6 months from the date prepared unless expiration is superceded by stock expiration. The CCV standards are prepared weekly.

8.3 All standards are stored at 2°-6° C.

8.4 Standard Solution Preparation

Table 8-2

STANDARD AND REAGENT PREPARATION

Standard Name	Stock	____ Amount of Added to ____	Final Concentration	Spike ID Type
PAH STD 5	PAH Calibration Intermediate Mix	200 µL of Intermediate plus 200 µL of acetonitrile	Refer to Table 8-3	
PAH STD 4	PAH Calibration Intermediate Mix	200 µL of PAH Calibration Intermediate Mix plus 600 µL of acetonitrile	Refer to Table 8-3	
PAH STD 3; CCV	PAH Calibration Intermediate Mix	100 µL of PAH Calibration Intermediate Mix plus 900 µL of acetonitrile	Refer to Table 8-3	
PAH STD 2	PAH Calibration Intermediate Mix	50 µL of PAH Intermediate Calibration Mix plus 950 µL of acetonitrile	Refer to Table 8-3	
PAH STD 1	PAH Calibration Intermediate Mix	10 µL of PAH Calibration Intermediate Mix plus 990 µL of acetonitrile	Refer to Table 8-3	
PAH Calibration Intermediate Mix	PAH Calibration Mix	1 mL of PAH Calibration Mix dilute to 5.0 mL with acetonitrile	0.2 x Table 8-1 values	
ICV Intermediate	PAH Reference Mix	100 µL of PAH Reference Mix plus 900 µL of acetonitrile	0.1 x Table 8-1 values	
PAH Spike	PAH Reference Mix (second source)	2.0 mL of PAH Reference Mix to 100 mL with methanol.	Acenaphthene 10 Acenaphthylene 10 Anthracene 1.0 Benzo(a)anthracene 1.0 Benzo(a)pyrene 2.0 Benzo(b)fluoranthene 2.0 Benzo(k)fluoranthene 2.0	

Table 8-2

STANDARD AND REAGENT PREPARATION

Standard Name	Stock	____ Amount of Added to ____	Final Concentration	Spike ID Type
			Benzo(g,h,i)perylene 5.0 Chrysene 5.0 Dibenzo(a,h)anthracene 2.0 Fluoranthene 10 Fluorene 20 Indeno(1,2,3-cd)pyrene 2.0 Naphthalene 10 Phenanthrene 10 Pyrene 10	
ICV	ICV Intermediate	100 µL ICV Intermediate plus 900 µL acetonitrile	Refer to Table 8-5	
PAH Terphenyl Surrogate Stock	Terphenyl d_{-14}	0.1 g terphenyl d_{-14} diluted to 500 mL with 1/1 methanol/acetonitrile	200 µg/mL	
PAH Terphenyl Surrogate Spike	PAH Surr Stock	2.0 mL of PAH Terphenyl Surrogate Stock diluted to 100 mL with methanol	4 µg/mL	AS1
DFB Surrogate Intermediate	DFB Stock Solution 1000 µg/mL	200 µL of DFB Stock Solution plus 800 µL of acetonitrile	200 µg/mL	
DFB Surrogate	DFB Stock Solution 1000 µg/mL	2.0 mL DFB Stock Solution diluted to 50 mL with methanol	40 µg/mL	AS2
DFB Level 5	DFB Surrogate Intermediate Solution	500 µL of Intermediate PAH plus 200 µL DFB Stock Intermediate Solution diluted plus 300 µL of acetonitrile	200 µg/mL	
DFB Level 4	DFB Surrogate Intermediate Solution	200 µL of DFB Stock Intermediate Solution plus 200 µL of acetonitrile	100 µg/mL	
DFB Level 3	DFB Surrogate Intermediate Solution	200 µL of DFB Stock Intermediate Solution plus 800 µL of acetonitrile	40 µg/mL	
DFB Level 2	DFB Surrogate Intermediate Solution	100 µL of DFB Stock Intermediate Solution plus 900 µL of acetonitrile	20 µg/mL	
DFB Level 1	DFB Surrogate Intermediate Solution	20 µL of DFB Stock Intermediate Solution plus 980 µL of acetonitrile	4 µg/mL	
MeNp STD 5	1-Methylnaphthalene 2-Methylnaphthalene Mix	200 µL of 1,2-MeNp diluted to 5 mL with acetonitrile	50 µg/mL	
MeNp STD 4	MeNp STD 5	100 µL of MeNp STD 5 plus 100 µL of acetonitrile	Refer to Table 8-4	
MeNp STD 3; CCV	MeNp STD 5	200 µL of MeNp STD 5 plus 800 µL of acetonitrile	Refer to Table 8-4	
MeNp STD 2	MeNp STD 5	100 µL of MeNp STD 5 plus 900 µL of acetonitrile	Refer to Table 8-4	
MeNp STD 1	MeNp STD 5	20 µL of MeNp STD 5 plus 980 µL of acetonitrile	Refer to Table 8-4	
1,2-MeNp Reference Intermediate (2nd source)	1-Methylnaphthalene 2-Methylnaphthalene	100 µL of 1-MeNp plus 100 µL of 2-MeNp plus 800 µL of acetonitrile	Refer to Table 8-4	
1,2-MeNp Reference Standard	1-Methylnaphthalene 2-Methylnaphthalene	50 µL of Intermediate plus 950 µL of acetonitrile	Refer to Table 8-4	

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Table 8-3

PAH CALIBRATION STANDARDS (µg/mL)

Parameter	PAH STD 5	PAH STD 4	PAH STD 3	PAH STD 2	PAH STD 1
Acenaphthene	50.0	25.0	10.0	5.0	1.0
Acenaphthylene	50.0	25.0	10.0	5.0	1.0
Anthracene	5.0	2.5	1.0	0.5	0.1
Benzo(a)anthracene	5.0	2.5	1.0	0.5	0.1
Benzo(a)pyrene	5.0	2.5	1.0	0.5	0.1
Benzo(b)fluoranthene	10.0	5.0	2.0	1.0	0.2
Benzo(g,h,i)perylene	25.0	12.5	5.0	2.5	0.5
Benzo(k)fluoranthene	10.0	5.0	2.0	1.0	0.2
Chrysene	25.0	12.5	5.0	2.5	0.5
Decafluorophenyl (DFB)	200.0	100.0	40.0	20.0	4.0
Dibenzo(a,h)anthracene	10.0	5.0	2.0	1.0	0.2
Fluoranthene	50.0	25.0	10.0	5.0	1.0
Fluorene	100.0	50.0	20.0	10.0	2.0
Indeno(1,2,3-cd)pyrene	10.0	5.0	2.0	1.0	0.2
Naphthalene	50.0	25.0	10.0	5.0	1.0
Phenanthrene	50.0	25.0	10.0	5.0	1.0
Pyrene	50.0	25.0	10.0	5.0	1.0
p-Terphenyl-d_{14}	20.0	10.0	4.0	2.0	0.4

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Table 8-4

MeNp CALIBRATION STANDARDS (µg/mL)

Parameter	MeNp STD 5	MeNp STD 4	MeNp STD 3	MeNp STD 2	MeNp STD 1
1-Methynaphthalene	50	25	10	5	1.0
2-Methynaphthalene	50	25	10	5	1.0

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Table 8-5

INITIAL CALIBRATION VERIFICATION

Parameter	Concentration (µg/mL)
Acenaphthene	5.0
Acenaphthylene	5.0
Anthracene	0.5
Benzo(a)anthracene	0.5
Benzo(a)pyrene	1.0
Benzo(b)fluoranthene	1.0
Benzo(g,h,i)perylene	2.5
Benzo(k)fluoranthene	1.0
Chrysene	2.5
Dibenzo(a,h)anthracene	1.0
Fluoranthene	5.0
Fluorene	10.0
Indeno(1,2,3-cd)pyrene	1.0
Naphthalene	5.0
Phenanthrene	5.0
Pyrene	5.0

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9.0 PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Table 9-1

HOLDING TIMES

Matrix	Client/ Project	Preparation from Collection (Days)	Analysis from Preparation (Days)	Container Type and Preservative
Solid	Standard	14	40	Store samples in a secure area at 2°-6° C
Water	Standard	7	40	Store samples in a secure area at 2°-6° C

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10.0 PROCEDURE

10.1 Instrument Conditions and Maintenance

10.1.1 Degas with helium.

10.1.2 For the Keystone column: Initial 60/40 - water:acetonitrile, linear gradient elution to 100% acetonitrile over 20 minutes at 1.0 mL/min. flow rate. Run 100% acetonitrile until the end of the run at 28 minutes. Column temperature 28° C.

10.1.3 For the Phenomenex column: Isocratic elution for 5 minutes using 60:40 water:acetonitrile, then linear gradient elution to 100% acetonitrile from 4-12 minutes at 1.0 mL/min flow rate. Run 100% acetonitrile until the end of the run at 28 minutes. Column temperature 28° C.

10.1.4 Both analytical columns have 10 minutes post-run time to allow for equilibration of the column conditions, back to initial conditions.

10.2 Initial Calibration

10.2.1 Record all standard preparations in the standard prep logbook.

10.2.2 Retention time windows under normal operating conditions are set at 2%, based on the retention time of the analytes in the calibration table. The table is updated daily for retention time using the retention time of the daily calibration standard. (The 2% window is slightly greater than statistically determined retention time windows that is determined annually).

10.2.3 Analyze and prepare a calibration curve using the standards as described in Tables 8-3 and 8-4. Inject these standards in order of increasing concentration. The calibration standards are reported in µg/mL.

10.2.4 Calculate the ratio of the response to the amount injected, defined as the calibration factor (CF), for each analyte at each standard concentration.

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

10.2.5 Calculate the mean calibration factor for all compounds and surrogates. Calculate the % Relative Standard Deviation (%RSD) of the CF_x values for the initial calibration using the following equations:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(CF_i - \overline{CF}_x\right)^2}{n-1}} \qquad \%RSD = \frac{SD}{\overline{CF}_x} \cdot 100$$

where:

SD = Standard derivation using sample population (n-1).
CF_x = Mean CF for each compound "x."
CF_i = Calibration factor for each calibration level "i" for the compound "x" of interest.
n = Number of calibration levels.

10.2.6 If the % RSD of any compound is 20% or less, linearity through the origin is assumed and the calibration factor is assumed to be constant over the calibration range, and the mean calibration factor may be used for quantitation.

10.2.7 If any analytes are greater than the 20% RSD, the initial calibration is valid as long as no one analyte is greater than 40% RSD and the mean of the RSD values for all analytes in the calibration is less than 20%. Note: The analyst and the data user must be aware that the use of the approach listed in this section (i.e., the average of all RSD values ≤ 20%) will lead to greater uncertainty of those analytes for which the RSD is greater than 20%. T he analyst and the data user should review the associated quality control results carefully, with particular attention to the matrix spike and laboratory control sample results to determine if the calibration linearity poses a significant concern. If this approach is not acceptable for a particular application, then the analyst may need to adjust the instrument operating conditions and/or the calibration range until the RSD is ≤ 20%, or apply a regression analysis.

10.2.7.1 The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project.

10.2.7.2 The data user must be provided with either a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded 20% and the results of the mean RSD calculation.

10.2.8 If the RSD of the calibration or response factors is greater than 20% over the calibration range, then linearity through the origin cannot be assumed. The analyst may then utilize a linear regression equation that is not forced through the origin.

10.2.9 Linear regression can also be used for analytes that do meet the RSD limits in Section 10.2.6. Calibration is valid when the regression calculation generates a correlation coefficient for each compound of interest greater than or equal to 0.995.

10.2.10 If the linear correlation coefficient is <0.995, a second order curve may be used if at least 6 calibration standards are used. If the coefficient of determination of the second order curve is ≥0.990, use this second order curve for quantitation of the compound of interest. Additional concentration levels of standards **are required** for higher order curves. Refer to Method 8000 for guidance. Do not apply higher order curves without consulting the supervisor.

10.2.11 If initial calibration requirements mentioned in the above sections cannot be met, then calibration is not valid and, therefore, the analyst should check instrument operation conditions and recalibrate.

10.2.12 Analyze a reference standard from a second source (ICV) immediately following an initial calibration to verify the curve. The curve is deemed acceptable provided each analyte in the reference standard calibration is within 15% difference of the mean calibration factor or within 15% of the theoretical concentration, depending on whether quantitation will be by mean calibration factor or from regression analysis, respectively.

10.2.13 If the ICV and the continuing calibration verification are used at the same concentration, then after each initial calibration and ICV analyze an additional standard that is of a different concentration.

10.2.14 Quantitation of samples must continue to be done using the procedure initially used.

10.3 Daily Calibration and Continuing Calibration Verification

10.3.1 The working calibration curve or calibration factor must be verified after the initial curve, at the beginning of the analytical sequence, and if a lapse in time >12 hours has occurred from last continuing standard.

10.3.2 A calibration check standard (continuing calibration verification) equivalent to the mid-level calibration standard must be analyzed at the beginning of the analytical sequence and after no more than every 10 samples or no longer than 12 hours (PAH calibration mix PAH STD3; CCV).

10.3.3 Continuing calibration and daily calibration verifications must be judged against the quantitation method used at the start. That is, if using a curve, judge standards as acceptable if $\leq \pm$ 20% Drift of their true value; if using the mean calibration factor, judge standards' calibration factor as acceptable if $\leq \pm$ 20% difference against the mean calibration factor.

Calculate % Drift and % Difference using the equations below. When using a curve:

$$\%\ \text{Drift} = \frac{\text{Calculated Conc.} - \text{Theoretical Conc.}}{\text{Theoretical Conc.}} \cdot 100$$

When using mean calibration factor:

$$\%\ \text{Difference} = \frac{\text{CF Verification Standard} - \overline{CF}_X}{\overline{CF}_X} \cdot 100$$

10.3.4 If the mean calibration factor is used for quantitation, then the calibration factor of the analyte must be ≤ 15% difference from the mean calibration factor.

10.3.5 If the regression curve is used for quantitating analytes in samples, then the concentration of the analyte in the calibration check standard must be ≤ 20% drift from the theoretical concentration (i.e., 80%-120% recovery).

10.3.6 If the percentage difference or drift is greater than 20% for one or more analytes, the standard is acceptable provided no one analyte %D exceeds 30% and the mean of all analytes' %D in the standard is 20% difference. However, the discussion in Section 10.2.7 applies.

10.3.7 Instrument blanks (acetonitrile) are allowed before CCV to verify the analytical system does not contain carryover into the CCV to avoid invalidation of the curve due to random carryover. Indication of carryover from one sample to another requires reanalysis of the potentially contaminated sample only.

10.4 Calibration Verification Corrective Action

10.4.1 If initial or continuing calibration criteria is not met, stop sample analysis immediately. Inspect the system. Minor corrective action may be performed such as changing the septum or injection port liner.

10.4.2 If after the minor corrective action a compliant CCV is analyzed, sample analysis may continue. Any samples not bracketed by valid CCVs must be reanalyzed and bracketed by compliant CCVs.

10.4.3 If minor corrective action does not fix the problem, major corrective action may be taken such as cleaning the injection port, cleaning the detector, or installing new columns. If major corrective action is taken, a new calibration curve must be run and all associated samples reanalyzed.

10.5 Sample Analysis

10.5.1 Once a successful initial calibration is complete, the primary analytical daily or batch sequence may begin (see Table 10-1).

Table 10-1			
DAILY RUN SEQUENCE			
Instrument Blank (acetonitrile)			
CCV (PAH STD 3) Standard			
Samples, including QC samples, not to exceed 10 samples or 12 hours			
CCV			
Samples, including QC samples, not to exceed 10 samples or 12 hours			
CCV			
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10.5.2 Analyze an instrument blank (acetonitrile) once each day to demonstrate an acceptable background. If background is not acceptable (i.e., all analytes <PQL), perform maintenance and reanalyze instrument blank.

10.5.3 Analyze CCV. The CCV must meet criteria in Section 10.3 and Table 12-1.

10.5.4 Filter the sample extract through a 13-mm 0.2-µm PTFE using a 5-mL syringe.

10.5.5 Inject the filtered extract onto the HPLC column using a 25-µL injection volume.

10.5.6 Quantitate based on the initial calibration procedure used.

10.5.7 If any analyte is detected in a sample at a level that exceeds the linear range of the calibration curve, the sample must be diluted to within the calibrated range. The dilution of samples may also be required to bring the chromatogram on scale even when no analytes of interest are detected.

10.5.8 Instrument blanks (acetonitrile) may be interspersed throughout the analytical run to check for carryover or when the system is run unattended (autosampler).

10.5 Confirmation Analysis (see Section 13 for project-specific requirements)

10.5.1 Fluorescence detection is not considered a confirmatory tool. No second dissimilar column is currently available.

10.5.2 Flag all positive PAH results as "N: Not confirmed with a second column."

10.5.3 Confirmation may be available from another technique if concentrations are at sufficient levels for detection, e.g., by GCMS.

11.0 DATA REDUCTION/EVALUATION/REPORTING

11.1 The instrument printout for processed samples is in µg/kg or µg/L if appropriate weights and volumes are used. The equations below are based on quantitation versus the curve and are provided as a check.

Soil Samples

$$\mu g/kg = \left[\frac{A_X - b}{m}\right]\frac{V}{S} \cdot 1000$$

where:

A_x = Response of analyte in sample (area).
B = Curve intercept (area).
m = Slope of curve (area/conc.; conc. in µg/mL).

S = Mass of sample, g.
V = Final volume of acetonitrile extract (mL).
1000 = Conversion factor, 1000 g/kg.
Bracketed term = Concentration (µg/mL) on curve associated with area A_x.

Typically, S = 30 g; V = 1.0 mL

Water Samples

$$\mu g/L = \frac{[A_x - b]}{[m]} \frac{V}{V_s}$$

where:

A_x = Response of analyte in sample (area).
B = Curve intercept (area).
m = Slope of curve (area/conc.).
V_s = Volume of sample extracted, L.
V = Final volume of acetonitrile extract (mL).

Commonly, V_s = 1 L; V = 1 mL.

11.2 For all spiked samples:

$$\% \text{ Recovery} = \frac{\text{Amount Determined}}{\text{Amount Added}} - \text{Amount found in original} \cdot 100$$

Table 11-1

TARGET ANALYTES AND QUANTITATION LIMITS

Analyte	Water PQL (µg/L)	Soil PQL (µg/Kg)
Acenaphthene	1	80
Acenaphthylene	1	80
Anthracene	0.1	3.33
Benzo(a)pyrene	0.2	6.67
Benzo(a)anthracene	0.1	3.33
Benzo(b)fluoranthene	0.2	6.67
Benzo(g,h,i)perylene	0.5	16.7
Benzo(k)fluoranthene	0.2	6.67
Chrysene	0.5	16.7
Dibenzo(a,h)anthracene	0.2	6.67
Fluorene	2	66.7
Fluoranthene	1	33.3
Indeno(1,2,3-cd)pyrene	0.2	6.67
Naphthalene	1	33.3

Table 11-1

TARGET ANALYTES AND QUANTITATION LIMITS

Analyte	Water PQL (µg/L)	Soil PQL (µg/Kg)
Phenanthrene	1	33.3
Pyrene	1	33.3

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Table 11-2

CUSTOM ANALYTES AND QUANTITATION LIMITS

Analyte	Water PQL (µg/L)	Soil PQL (µg/Kg)
1-Methylnaphthalene	1.0	
2-Methylnaphthalene	1.0	

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12.0 QUALITY CONTROL/QUALITY ASSURANCE/CORRECTIVE ACTION

Table 12-1

ROUTINE QUALITY CONTROL SAMPLES

QC Type	Frequency	Preparation Instructions	Acceptance Criteria	Corrective Action
ICV	After an initial calibration	See Table 8-2	85%-115%	Take corrective action; repeat calibration.
Method Blank	1 per batch of 20 or fewer samples	Refer to SOP EXT.13 (water) or EXT.25 (soil)	<PQL target compound, acceptable surrogate recovery.	If >PQL, reextract samples with concentration above PQL and which are < 10 times the blank concentration. If surrogate failure, reextract batch.
CCV	Every 10 samples and at the end	See Table 8-2	80%-120% recovery	Take corrective action; repeat analysis from last acceptable CCV.
MS/MSD	1 per batch of 20 or fewer samples	Refer to SOP EXT.13 (water) or EXT.25 (soil)	Project requirements if specified. Compare against LCS limits for bias.	Evaluate results in conjunction with other QC information to determine the effect of the matrix on the bias of the analysis. Comment, if appropriate, in narrative.
LCS	1 per batch of 20 or fewer samples	Refer to SOP EXT.13 (water) or EXT.25 (soil)	By reference, laboratory test code specification.	Reextract and reanalyze the entire batch.
Surrogate	All samples	Refer to SOP EXT.13 (water) or EXT.25 (soil).	By reference, laboratory test code specification.	Reextract and reanalyze sample.

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Table 12-2

CONTROL LIMITS FOR ROUTINE QUALITY CONTROL SAMPLES

QC Type	Parameters Charted	Type of Samples Charted	Source of Limits	Frequency Updated
Surrogate	Terphenyl-d_{14} Decafluorobiphenyl	Water/Soil	ASC limits	Annual
LCS	See Table 12-4	Water/Soil	ASC limits	Annual

Table 12-2

CONTROL LIMITS FOR ROUTINE QUALITY CONTROL SAMPLES

QC Type	Parameters Charted	Type of Samples Charted	Source of Limits	Frequency Updated
Revision: 7	Status: Final	Method: 8310	Minor Revision Date: 4/5/04	

Table 12-3

ACCEPTANCE CRITERIA FOR ROUTINE QUALITY CONTROL SAMPLES

QC Type	Parameter	Matrix	Spike Amount Water (ug/L)	Spike Amount Soil (ug/kg)	Recovery (%)
Surrogate	Terphenyl-d_{14}	Water/Soil	4	133.3	See Table 12-1
Surrogate	Decafluorobiphenyl	Water/Soil	40	133.3	See Table 12-1
Revision: 7	Status: Final	Method: 8310	Minor Revision Date: 4/5/04		

Table 12-4

ACCEPTANCE CRITERIA FOR ROUTINE QUALITY CONTROL SAMPLES

QC Type	Parameter	Matrix	Spike Amount Water (ug/L)	Spike Amount Soil (ug/kg)	Recovery (%)
LCS	Acenaphthene	Water/Soil	10.0	333.3	See Table 12-1
	Acenaphthylene	Water/Soil	10.0	333.3	
	Anthracene	Water/Soil	1.0	33.3	
	Benzo(a)pyrene	Water/Soil	2.0	66.7	
	Benzo(a)anthracene	Water/Soil	1.0	33.3	
	Benzo(b)fluoranthene	Water/Soil	2.0	66.7	
	Benzo(g,h,i)perylene	Water/Soil	5.0	166.7	
	Benzo(k)fluoranthene	Water/Soil	2.0	66.7	
	Chrysene	Water/Soil	5.0	166.7	
	Dibenzo(a,h)anthracene	Water/Soil	2.0	66.7	
	Fluoranthene	Water/Soil	10.0	333.3	
	Fluorene	Water/Soil	20.0	666.7	
	Indeno(1,2,3-cd)pyrene	Water/Soil	2.0	66.7	
	Napthalene	Water/Soil	10.0	333.3	
	Phenanthrene	Water/Soil	10.0	333.3	
	Pyrene	Water/Soil	10.0	333.3	
MS/MSD	Same as LCS	Water/Soil	Same as LCS	Same as LCS	
Revision: 7	Status: Final	Method: 8310	Minor Revision Date: 4/5/04		

13.0 SPECIAL PROJECT REQUIREMENTS

13.1 Jacobs; Otis requires LCS/LCSD.

13.2 U.S. Army Corps of Engineers (ACE)

13.2.1 Method Quantitation Limit (MQL) is between 3-10 times MDL. The low calibration standard concentration must be $\geq$3 times MDL. The Method Reporting Limit (MRL) may slide between two times the MDL and project-specific or regulatory requirements. Results below the MRL must be reported "ND." Results between the MQL and MRL must be reported as estimated (J flagged).

13.2.2 If using the grand mean approach for RSD (Section 10.2.7), no single analyte may be greater than 40% RSD.

13.2.3 If using linear regression, the correlation coefficient must be $\geq$0.995.

13.2.4 Initial Calibration Verification. The initial calibration curve shall be verified as accurate with a standard purchased or prepared from an independent source. This initial calibration verification (ICV) involves the analysis of a standard containing all of the target analytes, typically in the middle of the calibration range, each time the initial calibration is performed. The % recovery of each target analyte in the ICV is determined from the initial calibration and compared with the specifications for the CCV in each method (except for mercury by CVAA) as outlined in the Shell Document Tables 7 - 14.

Note for methods which report several (>5) target analytes, a small percentage of sporadic marginal failures may be tolerated (i.e., will not trigger reextraction and analysis of the entire batch). The number of target analytes reported for the method will dictate the number of allowable QC failures as given below.

Refer to the individual method tables for details on the implementation of this concept.

Number of Target Analytes	Number of Allowed Marginal Failures
5 - 15	1
16 - 30	2
31 - 45	3
46 - 60	4
61 - 75	5
76 - 90	6
91 - 105	7

The marginal failure allowance entails the application of an expanded acceptance criterion. If these QC criteria are not met, a new initial calibration must be performed.

13.2.5 For method blanks, check that no target compounds are found above one-half the required quantitation limit.

13.2.6 ACE criteria are summarized in Table 13-2.

Table 13-2

SUMMARY OF METHOD QUALITY OBJECTIVES FOR METHOD 8310

QC Element	Target Analyte/Surrogate	Sporadic Marginal Failure
Initial Calibration (ACE Shell Document Section 9.2.2.2)	Primary Evaluation: r $\geq$0.995, %RSD $\leq$20%, $r^2 \geq$0.990 Alternative Evaluation: Mean %RSD for all target analytes $\leq$20%	No allowance Alternative Evaluation: Maximum allowable %RSD for each target analyte <40%
ICV (ACE Shell Document Section 9.3/9.3.1)	%Rec = 85% - 115%	Sporadic Marginal Failures[1]: %Rec = 70% - 130%
CCV (ACE Shell Document Section 9.5/9.5.2/9.5.2.2)	Primary Evaluation: %Drift $\leq$15%, %D $\leq$15% Alternative Evaluation: Mean %Drift/%D for all target analytes $\leq$15%	No allowance Alternative Evaluation: Maximum allowable %Drift/%D for each target analyte $\leq$30%
MB (ACE Shell Document Section 10.2.1/1.4.1)	Analytes < MDL Check Sample (~2X MDL)	Not Applicable
LCS (ACE Shell Document Section 10.2.2/11.4.2)	Water: %Rec = 50% - 130% Solids: %Rec = 50% - 130%	Sporadic Marginal Failures[1]: %Rec = 30% - 150%

Table 13-2

SUMMARY OF METHOD QUALITY OBJECTIVES FOR METHOD 8310

QC Element	Target Analyte/Surrogate	Sporadic Marginal Failure
MS (ACE Shell Document Section 10.2.3/11.4.3/11.4.3.2)	%Rec = 40% - 140%	Sporadic Marginal Failures[1]: %Rec = 30% - 150%
MSD/MD (ACE Shell Document Section 10.2.4/11.4.4)	RPD ≤50%	RPD ≤60%
Surrogates (ACE Shell Document Section 10.2.5/11.4.5)	Interference-Free Matrix: Water: %Rec = 50% - 130% Solids: %Rec = 50% - 130% Project Sample Matrix: %Rec = 40% - 140%	Not Applicable

[1]The number of Sporadic Marginal Failure (SMF) allowances depend upon the number of target analytes reported from the analysis. Refer to Section 9.3 of ACE Shell Document for additional information on the application of sporadic marginal failures.

13.3 Illinois DOT

13.3.1 Fluorescence detection in series (low-level requirements).

13.4 AFCEE

13.4.1 Second column must be fully calibrated and results quantitative. The second column is an AFCEE requirement.

13.4.2 LCS must contain all target analytes.

13.4.3 All AFCEE projects are subject to project-specific variances.

13.4.4 Reporting

13.4.5 MDL may not be > 1/2 reporting limit (RL) unless a variance was obtained.

13.4.6 A calibration standard at or below the RL must be included.

13.4.7 Apply a "U" flag if analyte result <MDL; an "F" flag if MDL ≤ analyte result ≤ RL.

13.4.8 Calibration

13.4.9 All initial calibration curves, inorganic or organic, must be **verified with an independent source (vendor) standard** prior to sample analysis unless an independent vendor is unavailable and a variance was obtained.

13.4.10 The daily (organic) and continuing (organic and inorganic) calibration verifications are not required to be independent, however, the continuing calibration verification may not be used as the LCS (volatiles, mercury, any test without a preparation).

13.4.11 Batching

13.4.12 An AFCEE analytical batch is the environmental samples that are similar in composition (matrix) and are prepared at the same time and with the same **lot of reagents.**

13.4.13 A batch is not to exceed 20 samples. **The sample duplicate, MS, MSD are considered environmental samples; therefore, the actual number of unique samples is less than 20, AFCEE QAPP 3.0.**

13.4.14 Laboratory Control Sample

13.4.15 Laboratory Control Sample for solid must be prepared using **Ottawa sand** unless a variance was obtained.

13.4.16 The LCS must be prepared from second source material (Section 4.5.3. of AFCEE QAPP).

13.4.17 The LCSs must be spiked at a concentration ≤ the midpoint of the calibration curve for each analyte unless a variance was obtained.

13.4.18 Matrix Spike/Matrix Spike Duplicate

13.4.19 The MS and MSD must be spiked at a concentration ≤ midpoint of the calibration curve for each analyte unless a variance was obtained.

13.4.20 AFCEE samples must be used for spiking.

13.4.21 Surrogates (Organic analyses). A second surrogate, DFB, must be added for AFCEE. See tables for prepared values.

13.4.22 **Whenever one surrogate is outside limits,** corrective action must be performed.
13.4.23 When **retention time** is outside windows, perform corrective action.
13.4.24 Method blank must be less than RL unless a variance was obtained.
13.4.25 Holding times for analysis is calculated from the time of extraction completion to the time of completion of all **analytical runs including dilutions, confirmation, reanalyses.**
13.4.26 **AFCEE Project-Specific Method Requirements**
13.4.27 Retention times must be updated at each initial calibration and each calibration verification unless a variance was obtained.

13.5 Florida DEP

13.5.1 Analyze 1-methylnaphthalene and 2-methylnaphthalene and attendant QC.

Table 13-3

ACCEPTANCE CRITERIA FOR ROUTINE QUALITY CONTROL SAMPLES

QC Type	Parameter	Matrix	Spike Amount Water (ug/L)	Spike Amount Soil (ug/kg)	Recovery (%)
LCS	1-Methylnaphthalene	Water/Soil	4.5	150	See Table 12-1
	2-Methylnaphthalene	Water/Soil	4.5	150	
MS/MSD	Same as LCS	Water/Soil	Same as LCS	Same as LCS	
Revision: 7	Status: Final	Method: 8310	Minor Revision Date: 4/5/04		

14.0 ROUTINE MAINTENANCE

14.1 Document preventative maintenance in the maintenance log. Indicate 'As Found' condition or problem, the maintenance performed to correct the specific problem, and note the 'As Left' condition (i.e., that the problem was corrected). Initial, date.

Table 14-1

ROUTINE MAINTENANCE PROCEDURES

Equipment/ Instrument	Symptom	Operation	Frequency
HP1050 pump	High pressure	Replace in-line frit	As needed
HP1050 pump	High pressure	Replace in-line tubing	As needed
HP1050 auto sampler	High pressure	Replace injector capillary	As needed
HP1050 pump	Low pressure	Replace pump head seals	As needed
Revision: 7	Status: Final	Method: 8310	Minor Revision Date: 4/5/04

15.0 SAMPLE DISPOSAL

15.1 See waste disposal SOP A.10.

END OF SOP

Method 8082

TITLE: PCB Analysis by Method 8082		
Reviewer: K. Willy		Peer Reviewer: G. Hahn
Implementation Date: 6/13/01		Last Review Date: 8/29/02
Revision: 1	Status: Final	Method: 8082

1.0 SCOPE AND APPLICATION

1.1 This Standard Operating Procedure (SOP) describes the procedure for identifying and quantifying polychlorinated biphenyl compounds in surface waters, groundwater, soils, sediments, and oils by a gas chromatographic procedure.

2.0 METHOD SUMMARY

2.1 Extracts of water or soil samples (SOP EXT.4 or EXT.19) or dilutions of oils and wipes for PCB are analyzed on a gas chromatograph equipped with capillary columns and electron capture detectors. The GC is calibrated by injecting 5 levels of the analytes of interest and measuring response. An aliquot of a sample is injected into the GC and quantitative analysis is performed on the resulting chromatogram by comparing sample response to standard response. Qualitative Confirmation is accomplished by simultaneously injecting onto a second column.

2.2 The following deviations from the method are taken.

- **2.2.1** The target list of compounds usually reported by this method is listed in Table 11-1. This SOP does not cover use of this method for specific PCB congeners.
- **2.2.2** Minor changes in chromatographic conditions may be used to optimize separation and sensitivity.
- **2.2.3** DCB is the primary surrogate, TCMX is a secondary surrogate.
- **2.2.4** Due to the likelihood that one or more surrogates may be interfered with, the following criteria are applied.
  - **2.2.4.1** DCB in Laboratory Control Samples and method blanks must be recovered within in-house limits.
  - **2.2.4.2** DCB recovery will be determined for all samples; if recovery is outside in-house limits, TCMX recoveries will be evaluated and reported.
  - **2.2.4.3** Cases where both DCB and TCMX recoveries fail to meet criteria, and matrix effects are not evident, will require re-extraction and reanalysis of affected samples.

3.0 HEALTH AND SAFETY

3.1 All employees should protect themselves at a minimum with safety glasses, protective gloves, and a lab coat. For more information see the Analytical Services Center Chemical Hygiene Plan located in the QA Library Island shelf 2.

3.2 **Pollution Prevention** – Purchase chemicals based on expected usage, shelf life, and disposal cost. Prepare standard volumes on anticipated usage. Make appropriately sized dilutions and use serial dilutions where practical.

4.0 REFERENCES

4.1 SW-846 3rd Edition, Update III, June 1997, Methods 8000B, 8082, 3660B, 3665A.
4.2 Training SOPs QA.5 and A.23.
4.3 Data Review SOP A.25.
4.4 Laboratory Quality Assurance Manual (L-001).
4.5 MDL SOP A.18.
4.6 Corrective Action Procedure QA.1.
4.7 Initial and Peer Data Review checklist (C-055).

5.0 DEFINITIONS/ACRONYMS

5.1 MDL - Method Detection Limit as determined by 40 CFR Part 136, Appendix B.

5.2 PQL - Practical Quantitation Limit is the concentration above the MDL that can be reasonably obtained and is used as the limit of reporting (Table 11-1).

5.3 TCMX - Tetrachlorometaxylene.

5.4 DCB - Decachlorobiphenyl.

5.5 Aroclor 1660 – Shorthand notation for Aroclors 1016 and 1260 mixture.

6.0 INTERFERENCES/POTENTIAL PROBLEMS

6.1 Phthalates may cause false positives. Care should be exercised to reduce exposure of samples to plastics.

6.2 Elemental Sulfur – If present in the samples, may cause interferences. Sulfur clean-up using copper may be required. Refer to sulfur cleanup in SOP EXT.4 or SOP EXT.19.

6.3 Heavy baseline and organics in samples may be cleaned up using acid-partitioning (see Section 10.6.6).

7.0 INSTRUMENTATION AND EQUIPMENT

Varian 3400 or Hewlett Packard 5890 equipped with electron capture detector and autosampler
PE Nelson data system with TURBO*CHROM Software
Restek RTX CLPesticides, 30 m column x 0.53 mm 0.5 µm film (or equivalent)
Restek RTX CLPesticides II, 30 m column x 0.53 mm 0.42 µm film (or equivalent)
Volumetric flasks, Fisher or equivalent
Gastight syringes, Krackeler or equivalent
Screwcap vials with Teflon-lined septa, Krackeler or equivalent
Disposable Wiretrol® pipettes, Krackeler, Restek, or equivalent

8.0 REAGENTS AND MATERIALS

8.1 See Table 8-1, Summary of Standards, Reagents, and Consumables.

Table 8-1

SUMMARY OF STANDARDS AND REAGENTS

Description	Source	Concentration
AR1016/1260 MIX	Restek or equivalent	1000 µg/mL each
AR 1254 MIX	Restek or equivalent	1000 µg/mL
AR 1248 MIX	Restek or equivalent	1000 µg/mL
AR 1242 MIX	Restek or equivalent	1000 µg/mL
AR 1232 MIX	Restek or equivalent	1000 µg/mL
AR 1221 MIX	Restek or equivalent	1000 µg/mL
Pesticide Surrogate Mix	Restek or equivalent	200 µg/mL TCMX and 200 µg/mL DCB
Copper 30-40 Mesh	Supelco	Neat

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8.2 Standard Solution Preparation

8.2.1 All stock solutions commercially obtained shall be certified. Certificates are to be kept on file for all stocks received. All stocks and standards are to be stored at 2°-6° C or lower.

8.2.2 Stock standards expire one year from the date opened, unless an earlier vendor supplied expiration date supercedes.

8.2.3 Working standards expire six months from date prepared unless expiration is superceded by stock expiration.

8.2.4 Unopened stock standards expire per vendor-specified date; if not provided, 1 year from Date of Receipt.

Table 8-2

STANDARD AND REAGENT PREPARATION

Standard Name	Stock	____ Amount of Stock Diluted To _____	Final Concentration	Spike ID Type
Pest. Surr. Int.	Pesticide Surrogate Mix	50 µL to 10 mL hexane	10 µg/mL	
AR1660L	AR1016/1260 Mix Pest Surr. Int	2.5 µL plus 25 µL to 50 mL hexane	See Table 8-3	
AR1660ML	AR1016/1260 Mix Pest Surr. Int	5 µL plus 50 µL to 50 mL hexane	See Table 8-3	
AR1660M	AR1016/1260 Mix Pest Surr. Int	10 µL plus 100 µL to 50 mL hexane	See Table 8-3	
AR1660 MH	AR1016/1260 Mix Pest Surr. Int	20 µL plus 200 µL to 50 mL hexane	See Table 8-3	
AR1660H	AR1016/1260 Mix Pest Surr. Int	50 µL plus 500 µL to 50 mL hexane	See Table 8-3	
AR1254L	AR1254 Mix Pest Surr Int	2.5 µL plus 25 µL to 50 mL hexane	See Table 8-4	
AR1254ML	AR1254 Mix Pest Surr Int	5 µL plus 50 µL to 50 mL hexane	See Table 8-4	
AR1254M	AR1254 Mix Pest Surr Int	10 µL plus 100 µL to 50 mL hexane	See Table 8-4	
AR1254MH	AR1254 Mix Pest Surr Int	20 µL plus 200 µL to 50 mL hexane	See Table 8-4	
AR1254H	AR1254 Mix Pest Surr Int	50 µL plus 500 µL to 50 mL hexane	See Table 8-4	
AR1221L	AR1221 Mix Pest Surr Int	5 µL plus 25 µL to 50 mL hexane	See Table 8-5	
AR1221ML	AR1221 Mix Pest Surr Int	10 µL plus 50 µL to 50 mL hexane	See Table 8-5	
AR1221M	AR1221 Mix Pest Surr Int	20 µL plus 100 µL to 50 mL hexane	See Table 8-5	
AR1221MH	AR1221 Mix Pest Surr Int	40 µL plus 200 µL to 50 mL hexane	See Table 8-5	
AR1221H	AR1221 Mix Pest Surr Int	50 µL plus 500 µL to 50 mL hexane	See Table 8-5	
AR1232L	AR1232 Mix Pest Surr Int	2.5 µL plus 25 µL to 50 mL hexane	See Table 8-6	
AR1232ML	AR1232 Mix Pest Surr Int	5 µL plus 50 µL to 50 mL hexane	See Table 8-6	
AR1232M	AR1232 Mix Pest Surr Int	10 µL plus 100 µL to 50 mL hexane	See Table 8-6	
AR1232MH	AR1232 Mix Pest Surr Int	20 µL plus 200 µL to 50 mL hexane	See Table 8-6	
AR1232H	AR1232 Mix Pest Surr Int	50 µL plus 500 µL to 50 mL hexane	See Table 8-6	
AR1242L	AR1242 Mix Pest Surr Int	2.5 µL plus 25 µL to 50 mL hexane	See Table 8-7	
AR1242ML	AR1242 Mix Pest Surr Int	5 µL plus 50 µL to 50 mL hexane	See Table 8-7	
AR1242M	AR1242 Mix Pest Surr Int	10 µL plus 100 µL to 50 mL hexane	See Table 8-7	
AR1242MH	AR1242 Mix Pest Surr Int	20 µL plus 200 µL to 50 mL hexane	See Table 8-7	
AR1242H	AR1242 Mix Pest Surr Int	50 µL plus 500 µL to 50 mL hexane	See Table 8-7	
AR1248L	AR1248 Mix Pest Surr Int	2.5 µL plus 25 µL to 50 mL hexane	See Table 8-8	
AR1248ML	AR1248 Mix Pest Surr Int	5 µL plus 50 µL to 50 mL hexane	See Table 8-8	

Table 8-2

STANDARD AND REAGENT PREPARATION

Standard Name	Stock	____ Amount of Stock Diluted To _____	Final Concentration	Spike ID Type
AR1248M	AR1248 Mix Pest Surr Int	10 µL plus 100 µL to 50 mL hexane	See Table 8-8	
AR1248MH	AR1248 Mix Pest Surr Int	20 µL plus 200 µL to 50 mL hexane	See Table 8-8	
AR1248H	AR1248 Mix Pest Surr Int	50 µL plus 500 µL to 50 mL hexane	See Table 8-8	
AR1660 PCB Fish Spike	Aroclor 1016/1260	300 µL to 50 mL with methylene chloride. Good for 3 months.	6.0 µg/mL	P7
Pesticide/PCB Fish Surrogate	Pesticide Surrogate Mix	300 µL Pesticide Surrogate Mix to 100 mL with methylene chloride. Good for 3 months.	0.6 µg/mL	PS4

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Table 8-3

COMPONENTS AND CALIBRATION CONCENTRATIONS OF AR 1660 (1016/1260)

Compound	µg/mL				
	AR1660L	AR1660ML	AR1660M	AR1660MH	AR1660H
TCMX	0.005	0.010	0.020	0.040	0.100
AR1016	0.050	0.100	0.200	0.400	1.000
AR1260	0.050	0.100	0.200	0.400	1.000
DCB	0.005	0.010	0.020	0.040	0.100

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Table 8-4

AR1254 CALIBRATION LEVELS

Compound	µg/mL				
	AR1254L	AR1254ML	AR1254M	AR1254MH	AR1254H
TCMX	0.005	0.010	0.020	0.040	0.100
AR1254	0.050	0.100	0.200	0.400	1.000
DCB	0.005	0.010	0.020	0.040	0.100

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Table 8-5

FINAL CONCENTRATIONS (µg/mL) OF AR1221 – 5-POINT CALIBRATON

Compound	Level				
	Low	Med. Low	Med	Med High	High
TCMX	0.005	0.010	0.020	0.040	0.100
AR1221	0.100	0.200	0.400	0.800	1.000
DCB	0.005	0.010	0.020	0.040	0.100

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Table 8-6

FINAL CONCENTRATIONS (µg/mL) OF AR1232 - 5 POINT CALIBRATION

Compound	Level				
	Low	Med. Low	Med	Med High	High
TCMX	0.005	0.010	0.020	0.040	0.100
AR1232	0.050	0.100	0.200	0.400	1.000
DCB	0.005	0.010	0.020	0.040	0.100

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Table 8-7

FINAL CONCENTRATIONS (µg/mL) OF AR1242 - 5 POINT CALIBRATION

Compound	Level				
	Low	Med. Low	Med	Med High	High
TCMX	0.005	0.010	0.020	0.040	0.100
AR1242	0.050	0.100	0.200	0.400	1.000
DCB	0.005	0.010	0.020	0.040	0.100

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Table 8-8

FINAL CONCENTRATIONS (µg/mL) AR1248 - 5 POINT CALIBRATION

Compound	Level				
	Low	Med. Low	Med	Med High	High
TCMX	0.005	0.010	0.020	0.040	0.100
AR1248	0.050	0.100	0.200	0.400	1.000
DCB	0.005	0.010	0.020	0.040	0.100

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9.0 PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Table 9-1

HOLDING TIMES

Matrix	Client/Project	Preparation (Days)	Analysis (Days)	Container Type and Preservative
Water or Solid	Standard	Seven for water; 14 for soil.	The PCB extracts from sample preparation are to be analyzed within 40 days from extraction date.	Extracts are stored in a secure area in a separate refrigerator from original samples at 2°-6° C.
Water or Solid	NYSDEC	Five for water and soils from verified time of sample receipt.	The PCB extracts from sample preparation are to be analyzed within 40 days from extraction date.	Extracts are stored in a secure area in a separate refrigerator from original samples at 2°-6° C.

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10.0 PROCEDURE

10.1.1 The GC is equipped with two columns connected by a "Y" connector to one injection point and two electron capture detectors.

10.1.2 The carrier gas flow and temperature profile may vary somewhat to optimize analytical separation.

10.1.3 Recommended temperatures are set as follows: Injector = 200° C; Detector = 300° C Temperature program: Column Initial = 150° C. Initial Hold = 1.0 min. Column Rate = 5° C/min. Column Final = 280° C. Final Hold = minimum of 10 minutes and may be extended due to presence of late-eluting compounds in extracted samples.

10.1.4 The autosampler injects 1.0 µL of sample extract into each GC column (i.e., 2.0 µL total injection). Transfer of extracts to instrument autosampler vials shall be accomplished with disposable pipettes or graduated Wiretrol® micropipettes.

10.2 Establishing Retention Time Windows

10.2.1 Make three injections of mid level Aroclor 1016/1260 standard over 72-hour period.

10.2.2 Calculate the multicomponent retention time windows based on five peaks of the Aroclor 1016/1260 mixture. The windows will apply to all multicomponents. Pattern recognition is still the primary means of identification.

10.2.3 The retention time window is defined as plus or minus 3 times the standard deviation from the retention time of the initial mid-level standards in the continuing calibration sequence. However, analyst experience should weigh heavily. Pattern recognition should primarily be used for multi-response products.

10.2.4 Retain this data so that it can be easily retrieved.

10.2.5 To facilitate analyte identification, the retention time windows are set as percentages (±% realtime of daily calibration) into the data system. These values are slightly wider than calculated windows.

10.3 Initial Calibration

10.3.1 Compound list and Quantitation Limits (Table 11-1).

10.3.2 Analyze an instrument blank (hexane) to verify the analytical system does not contain carryover that will interfere with the identification or quantification of target compounds.

10.3.3 The initial calibration of PCBs is performed at the five levels identified with suffix L, ML, M, MH, and H (see Tables 8.3 - 8.8.). See Table 10-1 for specific calibrations.

10.3.4 Initial calibration for PCBs only require five-point calibration for AR1660 and a single point mid-level standard (AR1221M et al.) for Aroclors 1221, 1232, 1242, 1248, and 1254. Should any additional PCB be detected, or suspected, calibration must be verified for that Aroclor. If not verified, new initial calibration must be done for that Aroclor.

10.3.5 Note: Hexane = Instrument blank.

Table 10-1 INITIAL CALIBRATION SEQUENCE WITH AROCLORS 1660 (1016 AND 1260)
Hexane
AR1660L
AR1660ML
AR1660M
AR1660MH
AR1660H
AR1660 Reference (2nd source) (ICV)

See Section 10.3.4. Following AR1660 calibration, the instrument is recalibrated for any additional suspected or identified PCBs.

10.3.6 Inject 1.0 µL per column (i.e., 2 µL total injection) of each calibration standard. Tabulate area responses against the mass injected. The results are used to prepare a calibration curve for each analyte.

10.3.7 Calculate the ratio of the response to the amount injected, defined as the calibration factor (CF), for each analyte at each standard concentration.

$$\text{Calibration Factor (CF)} = \frac{\text{Total Area of Peaks *}}{\text{Mass Injected (in nanograms)}}$$

**Use the total area of the 5 largest peaks for quantitation. The number and specific peaks may need to be adjusted, depending if sample matrix interferences or pattern weathering exists(see Section 11.2).*

10.3.8 Calculate the mean calibration factor for all Aroclors and surrogates. Calculate the % Relative Standard Deviation (%RSD) of the CF_x values for the initial calibration using the following equations:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(CF_i - \overline{CF}_x\right)^2}{n-1}}$$

$$\%\,RSD = \frac{SD}{CF_x} \cdot 100$$

where:

SD = Standard derivation using sample population (n-1).
CF_x = Mean CF for each Aroclor "x."
CF_i = Calibration factor for each calibration level "i" for the Aroclor "x" of interest.
n = Number of calibration levels.

10.3.9 If the % RSD of any Aroclors is 20% or less, linearity through the origin is assumed and the calibration factor is assumed to be constant over the calibration range, and the mean calibration factor may be used for quantitation.

10.3.10 If any analytes are greater than the 20% RSD, the initial calibration is valid as long as no one analyte is greater than 40% RSD and the mean of the RSD values for all analytes in the calibration is less than 20% (Grand Mean approach). Note: The analyst and the data user must be aware that the use of the approach listed in this Section (i.e., the average of all RSD values ≤ 20%) will lead to greater uncertainty of those analytes for which the RSD is greater than 20%. The analyst and the data user should review the associated quality control results carefully, with particular attention to the matrix spike and laboratory control sample results to determine if the calibration linearity poses a significant concern. If this approach is not acceptable for a particular application, then the analyst may need to adjust the instrument operating conditions and/or the calibration range until the RSD is ≤ 20%, or apply a regression analysis.

10.3.10.1 The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project.

10.3.10.2 The data user must be provided with either a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded 20% and the results of the mean RSD calculation.

10.3.11 If the RSD of the calibration or response factors is greater than 20% over the calibration range, then linearity through the origin cannot be assumed. The analyst may then utilize a linear regression equation that is not forced through the origin.

10.3.12 Linear regression can also be used for analytes that do meet the RSD limits. Calibration is valid when the regression calculation generates a correlation coefficient for each analyte of interest greater than or equal to 0.995.

10.3.13 If the linear correlation coefficient is <0.995, a second order curve may be used if at least 6 calibration standards are used. If the coefficient of determination of the second order curve is ≥0.990, use this second order curve for quantitation of the analyte of interest. Additional concentration levels of standards **are required** for higher order curves. Refer to Method 8000 for guidance. Do not apply higher order curves without consulting the supervisor.

10.3.14 If initial calibration requirements mentioned in the above sections cannot be met, then calibration is not valid and, therefore, the analyst should check instrument operation conditions and recalibrate.

10.3.15 Analyze a reference standard from a second source (ICV) immediately following an initial calibration to verify the curve. The curve is deemed acceptable provided each analyte in the reference standard calibration is within 15% difference of the mean calibration factor or within 15% of the theoretical concentration, depending on whether quantitation will be by mean calibration factor or from regression analysis, respectively. The Grand Mean Approach may be used for the ICV except where instructed otherwise for specific clients. See Section 13.

10.3.16 Quantitation of samples must continue to be done using the procedure initially used.

10.3.17 When PCBs other than AR1016 or AR1260 are unexpectedly found at a given site, standard curves for those analytes must be run and checked against samples for pattern recognition. If positively identified, calibration must be established before samples can be quantified.

10.4 Daily Calibration and Continuing Calibration Verification

10.4.1 The working calibration curve or calibration factor must be verified at the beginning of the analytical sequence, and if a lapse in time >12 hours, has occurred from last continuing standard.

10.4.2 An instrument blank (hexane) is run to verify that the analytical system does not contain carryover that will interfere with the identification or quantification of target compounds

10.4.3 A calibration check standard equivalent to the mid-level calibration standard must be analyzed at the beginning of the analytical sequence and after no more than every 20 samples. Use AR1016/1260 mid-level (AR1660M).

10.4.4 Continuing calibration and daily calibration verifications must be judged against the quantitation method used at the start.

10.4.5 Calculate % Drift and % Difference using the equations below. When using a curve:

$$\%\,\text{Drift} = \frac{\text{Calculated Conc.} - \text{Theoretical Conc.}}{\text{Theoretical Conc.}} \cdot 100$$

When using mean calibration factor:

$$\%\,\text{Difference} = \frac{\text{CF Verification Standard} - \overline{CFx}}{\overline{CFx}} \cdot 100$$

10.4.6 If the mean calibration factor is used for quantitation, then the calibration factor of the analyte must be ≤ 15% difference from the mean calibration factor.

10.4.7 If the regression curve is used for quantitating analytes in samples, then the concentration of the analyte in the calibration check standard must be ≤ 15% drift from the theoretical concentration (i.e., 85-115% recovery).

10.4.8 If the percentage difference or drift is greater than 15% for one or more analytes, the standard is acceptable provided no one analyte %D exceeds 30% and the mean of all analytes' %D in the standard is ≤15% difference or drift (Grand Mean approach). However, the discussion in Section 10.3.10 applies.

10.4.9 Instrument blanks (hexane) are allowed before CCV to minimize chances for carryover into the CCV to avoid invalidation of the curve due to random carryover. Indication of carryover from one sample to another requires reanalysis of the potentially contaminated sample only.

10.5 Calibration Verification Corrective Action

10.5.1 If initial or continuing calibration criteria is not met, stop sample analysis immediately. Inspect the system. Minor corrective action may be performed such as changing the septum or injection port liner.

10.5.2 If after the minor corrective action a compliant CCV is analyzed, sample analysis may continue. Any samples not bracketed by valid CCVs must be reanalyzed and bracketed by compliant CCVs.

10.5.3 If minor corrective action does not fix the problem, major corrective action may be taken such as cleaning the injection port, clipping the column ends, baking out the detectors, or installing new columns. If major corrective action is taken, a new calibration curve must be run and all associated samples reanalyzed.

10.6 Sample Analysis

10.6.1 Once a successful initial calibration is complete, the primary analytical daily or batch sequence may begin (See Table 10-6).

Table 10-6 **DAILY CALIBRATION SEQUENCE WITH AROCLORS 1660 (1016 AND 1260)**
Instrument Blank
Aroclor 1660 M
Alternate PCBs as needed.
Samples, not to exceed 20, 10 recommended.
Aroclor 1660 M.
Alternate PCBs as needed.
Samples, not to exceed 20, 10 is recommended.
Repeat

10.6.2 After every 20 samples or less, an Aroclor 1660 mid-level standard is analyzed. If any PCB is detected in a sample at a level that exceeds the linear range of the calibration curve, the sample must be diluted to within the calibrated range.

10.6.2.1 Instrument blanks (hexane) may be interspersed throughout the analytical run to check for carryover or when the system is run unattended (autosampler).

10.6.3 Additional instrument blanks may be run after suspect samples or before standards to help eliminate matrix carryover.

10.6.4 Peak detection is prevented by the presence of elemental sulfur. Samples are copper treated prior to analysis; however, further treatment may be required for those samples that contain larger amounts of sulfur.

10.6.5 If samples are suspected to contain matrix interference (samples are colored) or after initial analysis samples have matrix interference, samples must under go sulfuric acid cleanup. This procedure is as follows.

10.6.6 Sulfuric Acid Cleanup

10.6.6.1 Using a disposable pipette, transfer 1 mL of the hexane extract to a 2-mL vial and, in a fume hood, carefully add 0.5 mL of the concentrated sulfuric acid. **Caution: Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.**

10.6.6.2 Cap the vial tightly and vortex for 30 seconds. Caution: Stop the vortexing immediately if the vial leaks. AVOID SKIN CONTACT, SULFURIC ACID BURNS.

10.6.6.3 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer, it should not be highly colored nor should it have a visible emulsion or cloudiness.

10.6.6.4 If a clean phase separation is achieved, proceed to Section 10.6.6.7.

10.6.6.5 If the hexane layer is colored or the emulsion persists for several minutes, remove the hexane layer from the vial and place in a 2.0-mL vial. Add another 0.5-mL portion of the clean sulfuric acid and perform another acid cleanup.

10.6.6.6 Vortex the sample for one minute and allow the phases to separate.

10.6.6.7 Analyze the hexane layer only.

10.7 Confirmation Analysis

10.7.1 Confirmation is not required by Method 8082.

10.7.2 If required by the client, a PCB is confirmed as present if the recognizable pattern is present on the confirmation column.

10.7.3 The confirmation analysis is <u>qualitative</u> only, unless quantitation is required by the client.

11.0 DATA REDUCTION/EVALUATION/REPORTING

11.1 If quantitating from a linear curve, the equation below is provided as a manual check.

$$\text{Concentration} = \text{mg/kg},\ \text{gg/} = \left[\frac{y-b}{m}\right]\frac{Vt}{S}\cdot Df$$

where:

y = Area of target analyte from initial curve.
b = Intercept (area).
m = Slope (area /[µg/mL]).
S = Mass of soil sample extracted in grams (g) or volume of water sample extracted in liters (L).
Vt = Final volume of the extract in milliliters (mL).
Df = Dilution factor. The dilution factor equals µL of extract used to make dilution + µL clean solvent used to make dilution divided by µL of extract used to make dilution.

11.2 Due to weathering effects or matrix interference, it is not always possible to quantitate samples using the same 5 peaks used in calibrating. All samples must be quantitated using a minimum of 3 peaks for each PCB and these same peaks from the calibration must be used to calculate concentrations. In cases where there are multiple PCBs detected, fewer peaks may be used. Peaks used for quantitation must be clearly identified on chromatograms of standards and samples.

Table 11-1

TARGET ANALYTES AND QUANTITATION LIMITS

Analyte	Soil PQL (µg/kg)	Water PQL (µg/L)
Aroclor-1016	20	0.50
Aroclor-1221	40	1.0
Aroclor-1232	20	0.50
Aroclor-1242	20	0.50
Aroclor-1248	20	0.50
Aroclor-1254	20	0.50
Aroclor-1260	20	0.50
TCMX	NA	NA
DCB	NA	NA

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Table 11-1.1

TARGET ANALYTES AND QUANTITATION LIMITS (WIPES)

Analyte	Wipe PQL (µg)
Aroclor-1016	1.5
Aroclor-1221	3.0
Aroclor-1232	1.5
Aroclor-1242	1.5
Aroclor-1248	1.5
Aroclor-1254	1.5
Aroclor-1260	1.5
TCMX	NA
DCB	NA

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Table 11-1.2

TARGET ANALYTES AND QUANTITATION LIMITS

Analyte	Oil PQL (µg/g)
Aroclor-1016	5
Aroclor-1221	10
Aroclor-1232	5
Aroclor-1242	5
Aroclor-1248	5
Aroclor-1254	5
Aroclor-1260	5
TCMX	NA
DCB	NA

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12.0 QUALITY CONTROL/QUALITY ASSURANCE/CORRECTIVE ACTION

12.1 Refer to the Quality Control Table below and the following sections for corrective actions.

12.2 Each sample is spiked with the surrogates DCB and TCMX. The DCB is the primary surrogate. Calculate its recovery. If peaks interfere with DCB, TCMX should be evaluated for acceptance. Proceed with corrective action when two surrogates are out of limits for a sample.

12.3 The sample is to be reextracted and reanalyzed unless it can be documented (chromatogram) that factors such as matrix effects are responsible. A corrective action report must be filed.

12.4 If any quality control criteria cannot be met, but the problem is correctable, the sample(s) affected must be reanalyzed.

12.5 Data that must be submitted with out of control events must be accompanied by a corrective action report.

12.6 If any criteria cannot be met, but the problem is correctable, the sample(s) affected must be reanalyzed.

Table 12-1

ROUTINE QUALITY CONTROL SAMPLES

QC Type	Frequency	Acceptance Criteria	Corrective Action
Method Blank	1 per preparation batch of 20 or fewer samples	< PQL	Reanalyze samples having concentrations > PQL.
Matrix Spike (MS) Matrix Spike Duplicate (MSD)	1 per preparation batch of 20 or fewer samples	Project requirements if specified. - Water 20% RPD - Soil 35% RPD	Project requirements if any, otherwise evaluate results in conjunction with other QC information to determine the effect of the matrix on the bias of the analysis. Comment in narrative if appropriate.
Laboratory Control Sample (LCS)	1 per extraction batch of 20 or fewer samples	Laboratory limits	Notify Project Manager immediately. Reextract and reanalyze the entire batch.
LCS Duplicate	Client Specified	Client specified	Client specified
Surrogate (SUR)	Every sample, blanks and QC sample	DCB must meet acceptance limits for method blanks and LCS samples. At least 1 surrogate must meet criteria in samples.	Reextract batch for blank or LCS failure. Reextract affected sample(s) unless matrix effect is evident from chromatogram.
Revision: 1	Status: Final	Method: 8082	Minor Revision Date: 9/11/03

Table 12-2

CONTROL CHARTED QUALITY CONTROL SAMPLES

QC Type	Analytes Charted	Matrix Charted
MS/MSD	Per client	Soil, Water, Oil, Wipes
LCS	Analytes per customer request	Soil, Water, Oil, Wipes
Surrogate (SUR)	DCB	Soil, Water, Oil, Wipes
Secondary Surrogate (SUR)	TCMX	Soil, Water, Oil, Wipes
Revision: 1 Status: Final	Method: 8082	Minor Revision Date: 9/11/03

13.0 SPECIAL PROJECT REQUIREMENTS

13.1 AFCEE

13.1.1 % Difference or drift may not be averaged.

13.2 U.S. Army Corps of Engineers (ACE)

13.2.1 Method Quantitation Limit (MQL) is between 3-10 times MDL. The low calibration standard concentration must be $\geq$3 times MDL. The Method Reporting Limit (MRL) may slide between two times the MDL and project-specific or regulatory requirements. The MRL may be higher or lower than the MQL. Results below the MQL must be reported as estimated (J flagged).

13.3 North Carolina DENR

13.3.1 If quantitating from a curve, a zero standard must be incorporated as well as five non-zero standards.

13.3.2 Alternate use of a midconcentration range continuing verification standard with a lower standard every 12 hours. The standard AR1660M is NOT at midconcentration of the calibration range.

13.3.3 Two MS/MSD pairs must be prepared and analyzed every 10 samples.

14.0 ROUTINE MAINTENANCE

14.1 Document preventative maintenance in the maintenance log. Indicate 'As Found' condition or problem, the maintenance performed to correct the specific problem, and note the 'As Left' condition (i.e., that the problem was corrected). Initial, date.

Table 14-1

ROUTINE MAINTENANCE PROCEDURES

Equipment/ Instrument	Symptom	Operation	Frequency
V3400/HP5890	Retention time shift	Change septum	Daily (or as needed)
V3400/HP5890	High baseline	Bake out column, detector	As needed
V3400/HP5890	Non-linear calibration	Replace detector; replace column	As needed
Revision: 1	Status: Final	Method: 8082	Minor Revision Date: 9/11/03

15.0 SAMPLE DISPOSAL

15.1 See waste disposal SOP A.10.

15.2 Waste containing $\geq$50 ppm total PCB must be segregated and identified as "PCB Waste."

END OF SOP

Method 3520C

TITLE: Extraction of PAH in Water for Subsequent Analysis by HPLC		
Reviewer: M. Davis		Peer Reviewer: G. Hahn
Implementation Date: 3/7/03		Last Review Date: 3/1/04
Revision: 3	Status: Final	Method: 3520/8310

1.0 SCOPE AND APPLICATION

1.1 Extraction/concentration of polynuclear aromatic hydrocarbons (PAH) in water samples for analysis by high performance liquid chromatography (HPLC).

2.0 METHOD SUMMARY

2.1 One liter of aqueous sample to which surrogate has been added is extracted in a continuous liquid-liquid extractor using methylene chloride. The methylene chloride extract is concentrated and solvent exchanged to acetonitrile.

3.0 HEALTH AND SAFETY

3.1 All employees should protect themselves at a minimum with safety glasses, protective gloves, and a lab coat. For more information see the Analytical Services Center Chemical Hygiene Plan located in the QA Library Island shelf 2.

3.2 Extraction concentration is performed in an operational fume hood.

3.3 All glassware should be inspected for defects (stains, cracks, bubbles, etc.) prior to each use. Do not use defective glassware.

3.4 **Pollution Prevention** – Purchase chemicals based on expected usage, shelf life, and disposal cost. Prepare standard volumes on anticipated usage. Make appropriately sized dilutions and use serial dilutions where practical.

4.0 REFERENCES

4.1 SW-846 Method 3520C, Method 8310.
4.2 Standard Operating Procedure LC.7 (Analysis Method 8310).
4.3 Training SOP QA.5 and A.23.
4.4 Data Review SOP A.25.
4.5 Laboratory Quality Assurance Manual (L-001).
4.6 MDL SOP A.18.
4.7 Corrective Action Procedure, QA.1.
4.8 GC and HPLC Surrogate/Spike Table (F-224).

5.0 DEFINITIONS/ACRONYMS

5.1 See general list located in the Quality Assurance Manual.

6.0 INTERFERENCES/POTENTIAL PROBLEMS

6.1 Interferences from dirty glassware can cause problems. Make sure glassware is clean before use.

7.0 INSTRUMENTATION AND EQUIPMENT

80-mm Drying funnel
Kuderna-Danish (K-D) Apparatus
Concentrator tube, 10-mL graduated
500-mL Evaporation flask (Kontes K-57001-500 or equivalent)
Snyder column, micro (569261-031 or equivalent)
Snyder column, 3 ball macro (Kontes K-503000-0121 or equivalent)
Boiling chips, solvent extracted (10/40 mesh Fisher or Equivalent)
Water bath heated with concentric ring cover capable of temperature control of ± 5° C
Full flow hood

Glass beads (hollow, 6-mm, Fisher Scientific)
Glass vials with screw cap PTFE-lined tops (2 mL)
pH test paper, universal (Whatman 2C13991 or equivalent)
Graduated cylinders (1 L)
Benchtop centrifuge (Fisher or equivalent)
PTFE centrifuge tubes
Pipettes (1 mL)
Class A volumetrics for standards preparation
Whatman 54 filter paper
Heating mantle and voltage regulator
Continuous liquid-liquid extraction chamber
Round bottom flask (500 mL)
Condensor
Contrad NF or equivalent
Pasteur pipettes

8.0 REAGENTS AND MATERIALS

8.1 See Table 8-1, Summary of Standards, Reagents, and Consumables.

Table 8-1

SUMMARY OF STANDARDS AND REAGENTS

Description	Source	Concentration	
Methylene chloride ($MeCl_2$),Ultra Resi Analyzed	J.T. Baker or equivalent	Neat	
Sodium sulfate – ACS Grade	J.T. Baker or equivalent	ACS specification	
Acetonitrile (HPLC grade), pesticide or equivalent	J.T. Baker or equivalent	Neat	
Methanol	J.T. Baker or equivalent	Neat	
PAH Terphenyl Surrogate (AS1)	GC (see SOP LC.7)	4 µg/mL	
PAH Spike (A1)	GC (see SOP LC.7)		µg/mL
		Acenaphthene	10
		Acenaphthylene	10
		Anthracene	1.0
		Chrysene	5.0
		Dibenzo(a,h)anthracene	2.0
		Benzo(a)anthracene	1.0
		Benzo(a)pyrene	2.0
		Benzo(b)fluoranthene	2.0
		Benzo(g,h,i)perylene	5.0
		Benzo(k)fluoranthene	2.0
		Fluoranthene	10
		Fluorene	20
		Indeno(1,2,3-cd)pyrene	2.0
		Naphthalene	1.0
		Phenanthrene	10
		Pyrene	10
Contrad NF	Fisher or equivalent	NA	
ASTM Type II Water	ASC System	NA	
Revision: 3 Status: Final	Method: 3520/8310	Minor Revision Date: None	

8.2 Standard Solution Preparation

Table 8-2

STANDARD AND REAGENT PREPARATION

Standard Name	Stock	____ Amount of Stock Added to ____	Final Concentration
1:1 (v/v) Methylene Chloride/ Acetone	Methylene chloride; acetone	Using a 1-L graduated cylinder, measure out a volume of acetone and add to a solvent bottle. Add the same volume of methylene chloride to the bottle. Do not shake the bottle with the cap on tight. Pressure may burst the bottle.	1:1 Methylene chloride, acetone
Ottawa or play sand		Baked at 120° C for 16 hours.	
Revision: 3	Status: Final	Method: 3520/8310	Minor Revision Date: None

9.0 PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Table 9-1

HOLDING TIMES

Matrix	Client/Project	Preparation (Days)	Analysis (Days)	Container Type and Preservative
Water	Standard	7 days from collection	40	2 1-L amber glass, refrigerated 2°-6° C
Water	NYSDEC	7 days VTSR	40	2 1-L amber glass, refrigerated 2°-6° C
Revision: 3	Status: Final	Method: 3520/8310		Minor Revision Date: None

10.0 PROCEDURE

10.1 Glassware Preparation

10.1.1 Manually wash all glassware in hot soapy tap water using Sparkleen or equivalent, or automatically wash using Contrad NF.

10.1.2 At a minimum, rinse manually washed glassware three times with tap water, followed by three times with ASTM Type II water.

10.1.3 If glassware still appears dirty, sonicate or clean with NOCHROMIX. Then rerun through the above cleaning procedure.

10.2 Preventing Contamination

10.2.1 Before use, rinse all glassware with acetone followed by methylene chloride.

10.2.2 Dry sodium sulfate (Na_2SO_4) (recommended 120° C, overnight or longer. Store in oven.). Rinse with methylene chloride before use.

10.2.3 Soxhlet extract any glass wool used.

10.3 Stock Solution Preparation

10.3.1 Prepare stock standard surrogate solutions in methanol or methylene chloride and using volumetric flasks and an analytical balance.

10.4 Sample Extraction Procedure

Each sample setup consists of a liquid-liquid extraction set and drying funnel. Set up the Waters Preparation Logbook. A witness must oversee the addition of all surrogates and spikes to the samples and QC. The witness must sign and date the observation in the logbook.

10.4.1 Sample Extraction Procedure – Continuous Liquid-Liquid (Method 3520C)

10.4.1.1 Add (approximately 500 mL) methylene chloride to the bottom of the extractor to a depth of at least one inch (1") above the bottom of side arm. Extractor should be attached to a round bottom flask containing three glass beads.

10.4.1.2 Sample Volume Measurement and Spike Addition

10.4.1.2.1 Mark the meniscus on the outside of the sample bottle. Record sample container number in prep log.

10.4.1.2.2 Add surrogate and/or spikes (Table 12-1) into bottle and shake. If the bottle lid does not have the PTFE lining, do not shake. Phthalate contamination may occur. Instead, let stand 10 minutes to equilibrate.

10.4.1.2.3 Transfer to extractor.

10.4.1.2.4 Rinse bottle with small volume of extraction solvent (methylene chloride), and add to extractor.

10.4.1.2.5 At completion of set up, add tap water to the mark on the sample bottle and measure the volume used (to the nearest 10 mL) by pouring into a graduated cylinder.

10.4.1.2.6 Record this as the sample volume. Record sample container number in prep log.

10.4.1.3 The 1-L bottles should not be assumed to hold 1000 mL if the level is at a certain height in the bottle. Volumes must be measured.

10.4.1.4 Should the container be significantly larger than the 1-L size (e.g., half-gallon jugs), then

10.4.1.4.1 Measure out 1000 mL of sample in a graduated cylinder. Record sample container number in prep log.

10.4.1.4.2 Add surrogate and/or spike while in graduated cylinder and let stand 10 minutes to equilibrate.

10.4.1.4.3 Transfer to extractor.

10.4.1.4.4 Rinse cylinder with small volume of extraction solvent (methylene chloride) and add to extractor.

10.4.1.5 LCS and Method Blank Spike Addition

10.4.1.5.1 Measure 1000-mL ASTM Type II water in a graduated cylinder.

10.4.1.5.2 Add surrogate and/or spike while in graduated cylinder and let stand 10 minutes to equilibrate.

10.4.1.5.3 Transfer to extractor.

10.4.1.5.4 Rinse graduated cylinder with small volume of methylene chloride and add to extractor.

10.4.1.6 Measure pH of sample using wide-range pH indicator strips. Record pH. Adjust pH to between 5-9 with 6N sodium hydroxide and/or 6N sulfuric acid. Record adjusted pH and lot number.

10.4.1.7 Take care that the sample does not spill over the side arm of the extraction chamber into the distilling flask. If it does, repeat the sample preparation. (Note: A layer of glass wool may be placed between the methylene chloride and sample if the sample contains a large amount of suspended solids that may precipitate.)

10.4.1.8 Attach condenser, turn on heating mantle, voltage regulator, and extract for a minimum of 18 hours but no more than 24 hours. Maintain methylene chloride drip rate at 10-15 mL per minute. Turn water on to an appropriate pressure.

10.4.1.9 At completion, turn off heating mantle and voltage regulator. Cool. Tip extractor to empty most of the methylene chloride into the distilling flask. Cover flask with foil.

10.5 Concentration Procedure

10.5.1 Kuderna-Danish Apparatus

10.5.1.1 Boiling chips are pre-rinsed with methylene chloride.

10.5.1.2 Assemble a Kuderna-Danish (K-D) apparatus by attaching a 10-mL concentrator tube containing a single boiling chip to a 500-mL evaporative flask.

10.5.1.3 Quantitatively transfer the extracts from the distilling flasks to the K-D; rinsing the flasks with 10-20 mL methylene chloride. Use a 80-mm funnel with Whatman 54 filter paper and 15-20 g of dried sodium sulfate.

10.5.1.4 Attach a 3-ball Snyder column and pre-wet by adding 1-2 mL methylene chloride. Place on a hot water (80°-90° C) bath and gently shake until bubbles appear. Adjust water temperature and vertical position to complete concentration in 15-20 minutes.

10.5.1.5 Concentrate to a volume of < 10 mL. Remove from steambath. Allow it to settle and cool (at least 10 minutes) to room temperature. At no time should the extract be allowed to go to dryness throughout the concentration procedure. If it does, re-extract the sample.

10.5.1.6 Turn steambath to ~95° C. Add fresh boiling chips and microcondensor concentrate to apparent volume of 2.0 mL. Add 4.0 mL acetonitrile and concentrate to final volume of 1.0 mL.

10.5.1.7 If during concentration, solvent vapor stops escaping from the Snyder column before the final volume is reached, this indicates that the extract contains large concentrations of high-boiling constituents. Concentration should be stopped and the extract brought to the nearest multiple of 5 mL final volume. Final volume should be noted accordingly in the Waters Preparation logbook.

10.5.1.8 Dry the outside of the joint between the concentrator tube and the K-D if condensation has formed. Remove concentrator tube, and provided large concentrations of high boiling constituents is not a problem, the sample can be further reduced.

10.5.1.9 Place concentrator tube in N-Evap water bath at 40° C. Using a gentle stream of nitrogen, blow the extract down to 1.0 mL. If necessary, adjust final volume to 1.0 mL with acetonitrile. (Note: The measurement of final volume is critical to the accuracy of the analysis.) Ensure that there is only one layer.

10.5.1.10 Place the extracts in labeled 2-mL vials with PFTE-lined caps and mark the meniscus. The marking ensures that the extract in the vial represents the final volume transferred and will indicate that no loss has occurred in storage. Record final extract volume.

10.5.1.11 If at any time a sample is lost during concentration (e.g., lost on steambath, spilled, etc.), note in extraction log and file a corrective action form notifying the project manager and supervisor.

10.5.2 Turbovap Concentration

10.5.2.1 Quantitatively transfer the extracts from the distilling flask to Zymark Turbovap tube as volume permits. Use a 80-mm funnel with Whatman 54 filter paper and 15-20 g of dried sodium sulfate.

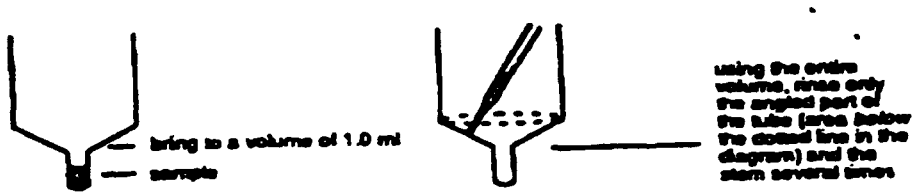
10.5.2.2 Place the tube in the Turbovap, set at 40° C (acceptable working range is from 38° C to 45° C) with a gentle stream of nitrogen.

10.5.2.3 Start the concentration. Remove the sample tube from the water bath when the beep signals. Failure to remove the tube promptly may result in analyte loss.

10.5.2.4 Add 10 mL acetonitrile and concentrate to final volume of 1.0 mL.

10.5.2.5 With a Pasteur pipette, add solvent to the 1-mL line.

10.5.2.6 Take the entire 1-mL sample into the Pasteur pipette and rinse the lower 25% of the Turbovap tube (i.e., 2 inches above the cone shape on the cylinder wall) 10 to 15 times.



10.5.2.7 Solvent evaporation during this rinsing will have reduced the volume. Add fresh solvent to bring the sample to 1 mL. Rinse the tube walls two more times and transfer the sample to an autosampler vial.

10.5.2.8 Concentrate to 1.0 mL (or nearest 5 mL if evaporation/concentration cannot be brought down to 1 mL).

10.5.2.9 Record the final volume in the notebook. Transfer the concentrated extracts to a 2-mL vial with PTFE-lined cap. Mark the meniscus. Label the vial. (Note: The measurement of final volume is critical to accuracy of the analysis.) Ensure that there is only 1 layer.

10.5.2.10 *If at any time a sample is lost during concentration (e.g., lost on steambath, spilled, etc.), note in extraction log and file a corrective action form notifying the project manager and supervisor.*

11.0 DATA REDUCTION/EVALUATION/REPORTING

11.1 Complete the batch in Khemia, fill out the concentration portion of the checklist and arrange for a peer review of the data. Place a copy of the extraction batch and checklist in the notebook in the instrument lab.

11.2 The entire extraction batch is placed in a storage box in the appropriate secure storage area at 2°-6° C.

12.0 QUALITY CONTROL/QUALITY ASSURANCE/CORRECTIVE ACTION

Table 12-1

ROUTINE QUALITY CONTROL SAMPLES

QC Type	Frequency	Preparation Instructions
Surrogate	Each sample, spike, blank, LCS	1.0 mL of PAH Terphenyl Surrogate (AS1) added to all samples and QC in sample container or graduated cylinder.
Matrix Spike (MS)	1 per 20 samples or fewer in batch. Must be reextracted if lost during concentration with the parent sample and MSD.	1.0 mL of PAH Spike (A1) added to sample container or graduated cylinder.
Matrix Spike Duplicate (MSD)	1 per 20 samples or fewer in batch. Must be reextracted if lost during concentration with parent sample and MS.	Same as matrix spike.
Laboratory Control Sample (LCS)	1 per batch	1.0 mL PAH Spike (A1) added to 1 L ASTM Type II Water in graduated cylinder.
Method Blank	1 per batch or minimum 1 per 20 samples	1 L ASTM Type II water.

Revision: 3	Status: Final	Method: 3520/8310	Minor Revision Date: None

13.0 SPECIAL PROJECT REQUIREMENTS

13.1 **IDOT** samples require low level detection limits - use 100 µL surrogate and 100 µL of spike solution. Do not use liquid-liquid extraction.

13.2 **AFCEE**

13.2.1 A batch is 20 environmental samples. These 20 samples *include* the MS/MSD or MS/MD for AFCEE 3.0.

13.2.2 Currently URS AFCEE projects require exactly 1-L sample. If sample bottle is <1000 mL, supplement with additional volume from another container. Note this additional container number and volume used in sample comments column on prep log page.

14.0 ROUTINE MAINTENANCE

14.1 Document preventative maintenance in the maintenance log. Indicate 'As Found' condition or problem, the maintenance performed to correct the specific problem, and note the 'As Left' condition (i.e., that the problem was corrected). Initial, date.

Table 14-1

ROUTINE MAINTENANCE PROCEDURES

Equipment/ Instrument	Symptom	Operation	Frequency
Steambath	Not heating	Replace heating coils	As needed
Fume Hood	No Draw	Contact Lab Manager	As needed

Revision: 3	Status: Final	Method: 3520/8310	Minor Revision Date: None

15.0 SAMPLE DISPOSAL

15.1 Follow waste disposal instructions in SOP A.10, Waste Disposal.

END OF SOP

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SOP No: F.1

Title: Sample Chain-of-Custody Procedures

Scope: This Standard Operating Procedure describes the Chain-of-Custody procedures to be followed by Laboratory Personnel.

1.0 SAMPLE RECEIPT CHAIN-OF-CUSTODY

The appropriate Chain-of-Custody procedures must be observed for all samples received. Samples received from the Sample Management Office (SMO) must have a complete Chain-of-Custody (COC) record, since these samples result in data which must be legally defensible. Therefore, the following procedures must be followed upon the receipt of samples.

1.1 Sample receipt and inspection shall be performed as described in SOP F.2, Sample Receipt, Inspection, Preservation and Storage Condition Requirements. The sample receipt shall be documented using the Sample Receipt Checklist, or for CLP samples CLP Form DC-1 (see SOP F.2, Sample Receipt, Inspection, Preservation and Storage Condition Requirements).

1.2 After completing the sample inspection and documentation process and finding no discrepancies, the original form is retained and included in the respective project file. Upon receipt, the client's Chain-of-Custody Form is signed by Sample Custodians to document time and date. A copy is returned to the client or designated sample management agency.

1.3 Samples shall be logged into the Laboratory Information Management System (LIMS) as described in SOP F.3 "Sample Logging and Record Keeping Procedures".

1.4 The Project Management Group shall be responsible for contacting the client (or SMO) to resolve any discrepancy or to report occurrences such as broken samples, improperly preserved samples, samples not listed on COC, insufficient sample volumes or inappropriate amounts or containers. The problem and the resolution shall be documented on the Sample Receipt Checklist Form.

2.0 LABORATORY CHAIN-OF-CUSTODY

Equally important to sample receipt Chain-of-Custody procedures is laboratory Chain-of-Custody documentation. Samples and sample extracts, digestates must be in custody of section supervisor or designated personnel at all times.

2.1 Samples are requested from Sample Control through the use of the Sample Request Form (Figure 1). These forms are available from Sample Control and are completed by the analyst requesting samples. The form requires that the person requesting the samples enter their name, the date, time the samples are needed, and the date of the request. This information is located at the top of the page. The samples requested are documented by entering the samples' GP Number and the analysis. The location block is completed by the analyst after a work order has been transmitted. Once custody of the samples has been transferred, the Sample Coordinator notes the date and time the sample request was completed and signs the form. The form is retained only for the purpose of review by the Sample Control personnel for use in assessing work load, and then may be discarded.

2.2 When a request for samples is received by Sample Control, the analyst shall first locate the samples requested as listed in the Sample Log Book. The LIMS Fraction Sheet (see SOP F.8, Sample Logging and Record Keeping) lists all samples in each individual work order and the assigned locations. Transfers are documented on the COC form. All samples can be found at the assigned locations unless transferred to lab personnel. Transfers shall be documented on the in house Chain-of-Custody Form (Figure 2). The Chain-of-Custody document serves as an effective means in determining sample locations.

2.3 Once determining that samples are available for transfer, the analyst locates and removes the samples before placing on workbench. The identification of the samples is checked against the Sample Request Form, and the LIMS Chain-of-Custody Form. If the samples do not match the Sample Request Form or the LIMS Chain-of-Custody Form, the identity question must be resolved before any transfer can take place. If there are no problems, the samples are transferred to the analyst.

2.4 To transfer the samples to the laboratory the following information must be completed on the LIMS Chain-of-Custody Form.

- Fraction Id

  Enter the sample fraction Id designation for the samples being transferred. Since Chain-of-Custody Forms are work order specific only the three digit sample identifier need be entered.

- Released By

  Enter the name of the Sample Custodian releasing the samples.

- Date/Time

  Enter the date and time of the transaction.

- Transferred To

  Enter the name of the person the samples are being transferred to.

2.5 When samples are returned to Sample Control the change in custody must again be documented. The identification of the samples is checked versus the Chain-of-Custody to verify sample identity. The following information is completed on the same line previously used when the samples were initially logged out.

- Accepted By

  Enter the name of the Sample Custodian receiving the samples.

- Date/Time

  Enter the date and time of the transaction.

- Disposition

  Enter the disposition of the samples, i.e. returned to sample location. Empty sample containers are taken to the disposal area for proper discard.

2.6 Laboratory personnel accepting samples must take full responsibility for those samples. Samples must remain under the custody of that individual, and shall not be transferred to another chemist without documentation on the proper forms (Figures 2 & 3).

2.7 When sample disposal is approved, or when a sample is completely consumed, the information shall be noted on the LIMS Chain-of-Custody Form. Empty sample containers should be returned to Sample Control for documentation and disposal.

3.0 TRANSFER OF SAMPLE CUSTODY TO ANOTHER LABORATORY

3.1 When it becomes necessary to sub-contract sample analyses to another laboratory, custody of the sample(s) must be transferred to that laboratory in the form of a Chain-of-Custody for Subcontracted Analysis (Figures 4 and 5). The forms are available in the Sample Control office. Sample control will complete the information on the Chain-of-Custody regarding the name and address of the lab and the sample information. The Sample Custodian/Coordinator must sign and date the form to release custody of the sample(s), and retain a copy of the form in the Chain-of-Custody record corresponding to the sample(s). The Chain-of-Custody will accompany the samples in the sealed container being shipped to the sub-contracted lab. The individual responsible for the custody of the sample(s) will sign and date the record, return the document to GPL Laboratories, addressed to the Sample Control office and/or project manager. The returned Chain-of-Custody shall be placed in the data package being sent to client.

Figure 1

GPL Laboratories, LLLP

Requested By: _____ **Date Requested:** _____

Date Needed: _____ **Time Needed:** _____

GPL Number	Analysis	Location	GPL Number	Analysis	Location

Request Filled By: _____ **Date/Time:** _____

Witnessed By (if applicable): _____

Figure 2

Date: 10/07/1998 Chain of Custody Page 1
GPL Laboratories, LLLP

Order: 9810040 Received: 10/07/1998 Received by: [illegible]

Samples: 18 # Containers: 2 Keep for: 90 days

Condition: OK

Sample Sign-Out				Sample Return		
Fraction	Released by	Date / Time	Released to	Accepted by	Date / Time	Disposition

Figure 3

SAMPLE EXTRACTION STORAGE AND CHAIN OF CUSTODY

Document Number:

Project Number	GP Work orders	No of Samples	Parameter	Released By	Released To	Released Date	Sample Custody to	Date	Returned By	Date Returned

Figure 4

Chain of Custody Form for Subcontracted Analyses

Page 1 of 1

GP Environmental Services, Inc.
202 Perry Parkway
Gaithersburg, MD 20877
(301) 926-6802
(301) 840-1209 (Fax)

GP P.O. No. [illegible]

GP P.O. No.________

Samples Transferred To:
____
____
____
Attn:________
Phone:________

GP Lab Sample ID	Field Sample ID	Date Sampled	Time Sampled	Sample Matrix	Analyses Required	Method	Type of Container	Preservative
1000???-01A	Sample 1	05/21/97		Water	[illegible]		[illegible]	

Carrier:________ Airbill No:________

Report Due On: 05/29/97 Send Report Attn:________ Perform Q.C. on Sample:________

Condition Upon Receipt:________

Comments:________

Samples Relinquished By:________ Date:______ Time:______ Samples Received By:________ Date:______ Time:______

Please complete this Chain-of-Custody Form immediately upon receipt, retain a copy for subcontracting laboratory records and return the original to: GP Environmental Services, 202 Perry Parkway, Gaithersburg, Maryland 20877.

Figure 5

CHAIN OF CUSTODY FORM FOR SUBCONTRACTED ANALYSES

Page___of___

GP Environmental Services, Inc.
202 Perry Parkway
Gaithersburg, MD 20877
(301) 926-6802
(301) 840-1209 (Fax)

GP W.O. No._____

GP P.O. No._____

Samples Transferred To:
_____
_____
_____
Attn:_____
Phone:_____

GP Sample No.	Sample ID	Date Sampled	Time Sampled	Sample Matrix	Analyses Required	No. of Containers	Type of Container	Preser-vative	Comments

Carrier:_____ Airbill No:_____

Report Due On:_____ Send Report Attn:_____ Perform Q.C. on Sample:_____

Condition Upon Receipt:_____

Comments:_____

Samples Relinquished By:_____Date:_____Time:_____Samples Received By:_____Date:_____Time:_____

Please complete this Chain-of-Custody Form immediately upon receipt, retain a copy for subcontracting laboratory records and return the original to: GP Environmental Services, 202 Perry Parkway, Gaithersburg, Maryland 20877.

SOP No: F.2

Title: Sample Receipt, Inspection, Preservation and Storage Conditions Requirements

Scope: This Standard Operating Procedure describes procedures to be used by Sample Control personnel in the inspection of incoming samples and the preservation and storage requirements of those samples.

1.0 SAFETY CONSIDERATIONS

1.1 When working with laboratory samples, safety must be of prime concern. It is required that safety glasses, a lab coat, and gloves be worn while unpacking or handling samples. Broken samples should be treated as a chemical spill and should be managed accordingly, using proper spill cleanup procedures (see SOP "Spill Cleanup"). Bench tops should routinely be covered with a bench liner, which should be changed as needed. Good personal hygiene procedures should be followed while in the Sample Control Area, specifically, it is recommended that hands be washed before or immediately after leaving the area, food or drink shall not be consumed, cosmetics shall not be applied, and smoking is forbidden in the Sample Control Area and throughout all areas of the building.

2.0 DOCUMENTATION OF INSPECTION

2.1 The inspection of all incoming sample shipments shall be documented on the Sample Receipt Checklist (Figure 1), except that those samples received under the Contract Laboratory Program shall be documented on CLP Form DC-1 (Figure 2). The Checklists shall be used to coordinate the inspection of the shipment and to record important information about the condition of the shipment and the documentation received.

2.2 The Sample Receipt Checklist documents the following information: The top section of the page documents receipt of the shipment, the identity of the client, the assigned Work Order Number and information relevant to the client's project. The next section of the checklist section contains specific items which must be checked and documented. Included in the section are spaces to document the sample and sample bottle count for comparison to the client supplied paper work and to document the necessity of a pH check, when applicable. If a pH check is

required, it shall be documented on the Sample Preservation Check Documentation Form (Figure 3).

2.3 The final section for comments is used to explain any problems or discrepancies with the shipment. Any "no" response to the previous section must be documented in the spaces provided. The sample control personnel will sign and date the form as indicated at the bottom of the page.

2.4 CLP Form DC-1 is used in the same manner as the Sample Receipt Checklist and shall be used in place of that form for the documentation of inspection of CLP sample shipments. All CLP samples received must be documented individually on Form DC-1.

2.5 The completed checklist is included with the original paper work submitted to the Project Management Group to be placed in the central project file. A copy of the completed Sample Receipt Checklist (or Form DC-1) is filed with copies of client supplied paper work, the Work Order and Chain-of-Custody documentation in the Sample Log book maintained by Sample Control.

2.6 Documentation of any problems or discrepancies associated with sample receipt is performed by the Sample Coordinator on the Sample Receipt Checklist (or Form DC-1). The Project Management Group is then informed of these items and is responsible in resolving the issues with the client. Resolution to any problems must be documented by the Project Management Group.

3.0 SAMPLE SHIPMENT RECEIPT

3.1 Each shipment of samples arriving by commercial carrier must be accompanied by an airbill, airbill sticker, or manifest. The Sample Coordinator (also referred to as the Sample Custodian for EPA CLP work), upon taking custody of the shipment, shall sign the airbill/manifest and record the date and time the shipment was received in the space provided on the document. If no space is provided, documentation may be recorded on any open space or the back of the document.

3.2 The Sample Coordinator shall next initiate a Sample Receipt Checklist or in the case of a CLP shipment, Form DC-1. The samples must be accompanied with a Chain of Custody (COC) document. The sample acceptance policy must include that:

A. The person submitting the sample must provide full documentation with the sample, which must include:

- Sample Identification
- The location, date and time of collection
- The collector name, preservative added
- Matrix
- Any special remarks concerning the sample

B Each sample or group of samples must include trip blanks, field blanks, equipment blanks, duplicates or other field submitted quality measures as required by the method.

C Each sample must show evidence of proper preservation and use of sample containers allowed by the test method.

D. Each sample must be of adequate volume for the requested testing.

Any deviation from the policy, the client will be contacted and documented. The sample(s) will not be processed.

Where required by method, pH of the samples must be determined and reported on the checklist. The client name, date and time received, the carrier name, and the name of the Sample Coordinator shall be recorded in the appropriate sections of the forms. The presence or absence of the airbill/manifest shall be documented and, if present, the airbill/manifest number shall be recorded. Then the temperature blank vial should be located, and the cooler temperature must be obtained by inserting the calibrated thermometer into the temp blank vial, and reading the temp after 60-90 seconds. If no temp blank exists then the thermometer must be inserted in the center of the cooler, where the samples are located, and the temp should be read after 60-90 seconds of thermometer insertion.

3.3 In the event that samples must be received on a weekend or holiday, special arrangements between the client and the laboratory must be established. Generally, clients must contact the Project Management Group to arrange for the proper presence. At that time Client Services shall ascertain if any samples requiring immediate analysis are to be included in the shipment. If this is the case, arrangements shall be made to have analytical staff available to perform the required analyses. Project Management Group shall arrange to have a person from Sample Control, or a properly trained alternate, available to receive the shipment. The shipment shall be received and inspected as per this procedure. The appropriate paperwork shall be completed and, if necessary, sample preservation shall be verified. Samples requiring immediate analysis are released upon receipt to the lab by the sample control personnel, before the completion of the transmission of the work order. Thereby enabling the laboratory to meet the required holding time criteria.

4.0 SHIPPING CONTAINER INSPECTION

4.1 All sample shipping containers shall be inspected for integrity and physical damage upon receipt. This shall be documented on Line 2 of the Checklist. Any problems found must be documented in the comments section at the bottom of the page. For Form DC-1, comments shall be made in the Remarks section.

4.2 Safety Note: If a strong smell is emanating from a shipping container, place the container in the hood to be unpacked. If a liquid is leaking from a shipping container, place container in the hood on a metal or plastic tray to contain the liquid and prevent gross contamination of the Sample Control Area. Any leaking material should be considered as a hazardous material and should be treated as such. All sample shipments originating from the Sample Management Office (SMO) for the

Contract Laboratory Program (CLP) must be opened and unpacked under the hood. In all cases, proceed with caution while checking for broken sample vessels.

4.3 Once the shipping container has been examined for damage, and the presence or absence of custody seals is determined. The sample receiving personnel will evaluate and document the use of chain of custody seals that are of the tamper evident variety. Then the overall condition should be ascertained. This check shall be documented in the appropriate spaces on the forms.

5.0 SAMPLE VESSEL INSPECTION

5.1 The shipping container shall be carefully opened, any paperwork should be removed, and it shall be determined whether ice or cold packs are present. The temperature of the shipping container shall be measured by placing a thermometer in the provided temp blank or among the samples, closing the lid and reopening the container and leaving the thermometer for approximately 60-90 seconds. On the sample receipt checklist, document the presence or absence of ice or cold packs and the temperature of the shipping container. Please note that if the samples do not require cold preservation, for example preserved water samples for metals analysis, "No" must be checked and an explanation of N/A included in the comments section.

5.2 The shipping container should be carefully unpacked and the incoming samples checked for:

- Physical damage due to inadequate packing and/or protection.

- Loss of sample due to inadequate and/or improper sealing of the sample container (i.e., leakage of liquids, loss of particulate material from filters, etc.).

- Possible contamination because of inadequate separation of sample types or bulk sample materials (i.e., charcoal tubes or VOA vials shipped in the same container as bulk liquid organics).

- Adequate containment of volatile organic samples and total organic halide samples in septum vials; there should be zero headspace. If headspace is found this shall be documented on Line 8 of the Checklist or noted in the sample Remarks section of Form DC-1 and the Project Manager/Client Services Group contacted, as the client may wish to re-sample.

- Proper use of special shipping procedures required to preserve the samples. For example, if shipping instructions note that samples are to be kept frozen, then samples should be frozen upon receipt.

If samples are broken or evidence that sample integrity may have been compromised, the incident shall be documented in the designated space of the Checklist and detailed in the Comments section. For CLP samples this shall be documented on Form DC-1, Line 8 and explained in the remarks section for the affected samples and shall also be noted on the Sample Traffic Report Form. The Project Management Group shall be notified of any such problems as soon as possible.

6.0 CONTRACT LABORATORY PROGRAM SAMPLE VESSEL INSPECTION

6.1 For samples submitted by SMO, a review of sample documentation is required once the shipping container has been unpacked. Each shipping container should possess a Chain-of-Custody Form and a Sample Traffic Report Form for the samples contained within the shipping vessel. Each sample should have a Sample Label and a Sample Tag attached to the bottle (where applicable). EPA sample bottles should also have a custody seal over the cap to detect tampering. All items shall be reviewed and documented on Form DC-1.

6.2 Presence or absence of custody seals should be determined. If present, condition of custody seals must be assessed. This shall be documented on Line 1 in the Remarks section of Form DC-1.

6.3 Presence of EPA Sample Tags on sample bottles should be determined. The presence or absence of tags shall be documented on Line 7.

6.4 It shall be determined if the EPA Traffic Report or SAS Packing list was included in the shipment. Documentation shall be made on Line 4.

6.5 It shall be determined if the Chain-of-Custody document was included in the shipment. Documentation shall be made on Line 3.

6.6 The Chain-of-Custody document shall be reviewed to verify the entry of Sample Tag numbers on the Chain-of-Custody. If tag numbers have not been recorded on the Chain-of-Custody, the Sample Coordinator shall perform the document entries and shall document the information in the remarks section for the affected sample.

6.7 The Chain-of-Custody shall be compared with the Sample Labels. Any discrepancies shall be documented. This shall be documented in the remarks section for the affected sample.

6.8 The Chain-of-Custody shall be compared with the Sample Tags. Any discrepancies shall be documented. This shall be documented in the remarks section for the affected sample.

6.9 The Chain-of-Custody shall be compared with the EPA Traffic Reports. Discrepancies shall be documented in the remarks section for the affected sample.

7.0 SAMPLE PRESERVATION INSPECTION

7.1 EPA Contract Laboratory Program (CLP) Samples

7.1.1 Samples which are submitted under the Contract Laboratory Program for inorganic parameters (metals and cyanide) are preserved in the field and may require pH adjustment. These samples are to be checked for proper preservation upon receipt. Because of the nature of these samples, proper safety precautions must be observed. Safety glasses, lab coat and disposable gloves shall be worn when handling the sample bottles while performing pH measurements. Gloves shall be changed when noted to prevent contamination between both the samples or of the employee.

7.1.2 The pH check shall be performed by removing an aliquot of the sample, pouring it into a small disposable container, depositing the aliquot onto a pH strip paper. Match the resulting color of the pH paper to the color scale provided with the pH paper.

Samples for metals analysis must have a pH of less than 2, and samples for cyanide must have a pH greater than 12.

7.1.3 Record the pH reading on a Sample Preservation Check Documentation Form (Figure 3). The pH may be recorded as less than the value required for acid preserved samples (i.e. <2), or greater than the required value for NaOH preserved samples (i.e. >12 for NaOH preserved cyanide samples). If the sample is discovered to be inadequately preserved, the exact pH reading from the pH check must be recorded. The form shall be signed and dated by the responsible person.

7.1.4 If the pH check indicates that the sample was not adequately preserved, contact the Project Manager immediately to receive instructions from the Sample Management Office. Documentation of sample preservation deficiencies, and instructions given by the Sample Management Office shall be documented in the case file and the case narrative by the Project Manager. If the Sample Management Office representative dictates that the samples shall be preserved in the laboratory, documentation of this activity shall be indicated on the Sample Preservation Check Documentation Form (Figure 3). The samples may be preserved by Sample Control or laboratory personnel, where applicable. In either case, suitable quantities of the appropriate preservative shall be added to the inadequately preserved samples. Documentation of these activities shall be indicated on the Sample Preservation Check Documentation Form (Figure 3). Copy of the documentation form shall be filed in the case file.

7.1.5 Table 1 provides information on required containers, holding instructions, and holding times for USEPA CLP submitted samples.

7.2 Commercial Samples

7.2.1 EPA requires chemical preservation of water samples to be analyzed for selected parameters. Table 2 presents information which lists parameters, required containers, sample size needed, preservation techniques and holding times for sample analysis performed by methods specified in 40 CFR Part 136, Test Methods for Evaluating Solid Waste - SW 846, and Methods for Chemical Analysis of Water and Wastes (MCAWW). The Sample Coordinator is responsible for verifying that any samples requiring pH adjustment have been appropriately preserved in the field.

7.2.2 The pH check shall be performed by using a strip of pH paper. Match the resulting color of the pH paper to the color scale provided with the pH paper.

7.2.3 Record the pH reading on a Sample Preservation Check Documentation Form (Figure 3). The pH may be recorded as less than the value required for acid preserved samples (i.e. <2), or greater than the required value for NaOH preserved samples (i.e. >12 for NaOH preserved cyanide samples). As an alternative a check mark may be used to signify that the sample met the preservation criteria. If a sample is discovered to be inadequately preserved the exact pH reading from the pH check must be recorded. The form shall be signed and dated by the responsible person.

7.2.4 If the pH check indicates that the sample was not adequately preserved, contact the Sample Control Supervisor immediately. The Sample Control Supervisor will contact the appropriate Project Manager who will, after consultation with the client, instruct the Sample Control Supervisor of the appropriate action to follow. Generally, the samples are preserved during that time and the necessary documentation of the problem and the resolution are performed. Also, notations are indicated in the final report describing the situation. Samples may be preserved by Sample Control or laboratory personnel. In either case, suitable quantities of the appropriate preservative shall be added to the inadequately preserved samples. See Table 2 for information on preservatives and criteria. Documentation of these activities shall be made on the Sample Preservation Check Documentation Form (Figure 3). Copy of the documentation form shall be filed in the case file.

Note: If drinking water metals samples are acidified in the laboratory, the time that the samples are acidified must be recorded on the preservation check form (Fig.3) in order to meet the 16 hour hold time requirement.

7.2.5 Failure to appropriately preserve the samples in the field may result in invalid analytical data. It is the responsibility of Project Management Group to advise the client of this potential.

All acid preservatives are verified upon arrival to the lab.

7.2.6 Samples for State of North Carolina, which are chlorine sensitive, i.e., organics, ammonia, TKN and cyanide must be checked for the presence of chlorine and treated, if required, before storage and analysis. Documentation of these activities shall be noted on the sample residual chlorine check form (Figure 4).

7.3 pH Adjustment Procedure

7.3.1 Samples which require pH adjustment must have appropriate amounts of the required preservative added. This procedure must be carefully performed and must be properly documented.

7.3.2 Generally, the preservative solutions are relatively concentrated (i.e. 1:1 Nitric or Sulfuric Acid, 5N NaOH) to avoid significant changes in volume. Therefore, only a small quantity of preservative should be added. Due to sample composition, proper safety precautions must be observed. While performing pH adjustments, safety glasses, lab coats and disposable gloves shall be worn. Gloves shall be changed when soiled to prevent sample contamination.

7.3.3 When a particular sample requires additional preservation the sample shall be opened and a small quantity of the preservative added. The amount of preservative added should be in increments of approximately 0.5ml/250ml of sample. Once the preservative is added the bottle shall be securely capped and shaken to distribute the preservative. The bottle shall then be carefully opened, and observed for evidence of escaping pressure before rechecking the pH. The pH check shall be performed by removing an aliquot of the sample, pouring it into a small plastic cup and depositing the drop onto a strip of pH paper. Match the resulting color of the pH paper to the color scale provided with the pH paper. If the pH does not yet meet the method specification, repeat the process until an acceptable value is maintained.

7.3.4 Documentation of the preservation adjustment shall be indicated on the Sample Preservation Adjustment Documentation Form (Figure 3). Each space shall be completed for each listed sample and the form shall be signed and dated by the responsible person.

7.4 Radiation Monitor

The radiological monitor meter will be used to screen samples at the client's request or the samples were specifically requested for radiological test (i.e., Alpha, Beta or Gamma)

7.4.1 To operate, install a fresh 9 volt alkaline battery. Take 5 min survey of background readings, then take the reading from the sample, range should be ±10% of the background reading. If it is off scale, document the reading and contact the project manager immediately who will consult with the client and appropriate action will be followed.

7.4.2 The monitor senses ionizing radiation by means of a Reagan Muller tube with a thin mica end window. The tube is fully enclosed inside the instrument.

7.4.3 When a ray or particle of ionizing radiation strikes the tube, it is [illegible] electronically and displayed by a flashing point light. When the switch is in the audio position, the instrument will also beep with each ionizing event.

7.4.4 Always keep the range switch in the [illegible] position (lowest) unless samples are expected to be measuring high levels of radiation.

7.4.5 Handle the [illegible] carefully. Avoid exposing to liquids, moisture and corrosive gases, also avoid extreme temperatures or direct sunlight for [illegible]

7.4.6 To avoid contamination, do not touch the instrument to the surface being [illegible]

7.4.7 The 4[illegible]D-4EC monitor have proven to be very reliable instruments. When calibration or servicing needed, contact the address below:

S.E. International, Inc.
P.O. Box 39
436 Farm Road
Summertown, TN 38483
Tel: (931) 964-3561
Fax: (931) 964-3564

Figure 1

SAMPLE RECEIPT CHECKLIST

W.O. No: _____

Client Name: _____

Date Received: _____

Time Received: _____

Received By: _____

Carrier Name: _____

Prepared (Logged In) By: _____ / _____
Initials Date

Project: _____

Site: _____

VOA Holding Blank I.D. No: _____

	YES	NO
Airbill/Manifest Present?	___	___
No. _____		
Shipping Container in Good Condition?	___	___
Custody Seals Present on Shipping Container?	___	___
Condition: Broken ____		
Intact-not dated or signed ____		
Intact-dated and signed ____		
Usage of Tamper Evident Type	___	___
Chain-of-Custody Present?	___	___
Chain-of-Custody Agrees with Sample Labels?	___	___
Chain-of-Custody Signed?	___	___
Packing Present in Shipping Container?	___	___
Type of Packing _____		
Custody seals on Sample Bottles?	___	___
Condition: Good ____ Broken ____		
Total Number of Sample Bottles ____		
Total Number of Samples ____		
Samples Intact?	___	___
Sufficient Sample Volume for Indicated Test?	___	___

	YES	NO
Trip Blanks: No. of Sets ____	___	___
Field Blanks: No. of Sets ____	___	___
Equip. Blank: No. of Sets ____	___	___
Field Duplicate: No. of Sets ____	___	___
MS/MSD: No. of Sets ____	___	___
VOA Vials Have Zero Headspace?	___	___
Preservatives added to Sample Bottles?	___	___
pH Check Required?	___	___
Performed By? _____	___	___
Ice Present in Shipping Container?	___	___

Container #	Temp.	Container #	Temp.
_____	____	_____	____
_____	____	_____	____
_____	____	_____	____
_____	____	_____	____
_____	____	_____	____
_____	____	_____	____
_____	____	_____	____

Project Manager Contacted?
Name: _____
Date Contacted: _____

Any NO response must be detailed in the comments section below. If items are not applicable to particular samples or contracts, they should be marked N/A/

COMMENTS: _____

_____

_____

_____

Checklist Completed By: _____

Date: _____

Figure 2

SAMPLE LOG-IN SHEET

Lab Name: ______________________________ Page ____ of ____

Received by (Print Name): ______________________ Log-in Date: __________

Received By (Signature): ______________________________

Case Number: ______________

Sample Delivery Group No.: ______________

SAS Number: ______________

REMARKS:

1. Custody Seal(s) — Present/Absent* Intact/Broken
2. Custody Seal No.: ______ ______
3. Chain-of-Custody Records — Present/Absent*
4. Traffic Reports or Packing List — Present/Absent*
5. Airbill — Airbill/Sticker Present/Absent*
6. Airbill No.: ______
7. Sample Tags — Present/Absent*
   Sample Tag Numbers — Listed/Not Listed on Chain-of-Custody
8. [illegible]
9. [illegible] — Yes/No*
10. [illegible] ______
11. [illegible] ______

SAMPLE TRANSFER

Fraction ______ ______

Area #: ______ ______

By ______ ______

On ______ ______

	CORRESPONDING		
EPA SAMPLE #	SAMPLE TAG #	ASSIGNED LAB #	REMARKS: CONDITION OF SAMPLE SHIPMENT, ETC.

*Contact SMO and attach record of resolution

Reviewed By: ______________

Date: ______________

Logbook No.: ______________

Logbook Page No.: ______________

FORM DC-1

Figure 3

Sample Preservation Check Documentation Form

WORK ORDER: ______________

Parameter: Preservative: pH Value	Metals HNO3 <2	Phenol H2SO4 <2	TPH O&G H2SO4 <2	Classical Parameters H2SO4 <2	Cyanide NaOH >12	Sulfide NaOH >9	Radiology H2SO4 <2	Other Parameters
CLIENT I.D.								

Sample Preservation Check Performed By: ______________ Date: ___________

Figure 4

North Carolina **Sample Residual Chlorine Check Form**

WORK ORDER:____________________

Client ID	Organics	TKN	Ammonia	Cyanide	Comments

Sample Check Performed by:_______ Date:________

Table 1
Summary of Contract Laboratory Program Required
Containers, Preservation Techniques, and Holding Times[1]

Parameter	Container	Holding Instructions	Maximum Sample Holding Time
Metals	P, G	Room Temperature	180 days from VTSR
Mercury	P, G	Room Temperature	26 days from VTSR
Cyanide (Total and amenable to chlorination)	P, G	Room Temperature	12 days from VTSR
Volatiles	G(TS)	Store at 4° ± 2°C	10 days from VTSR
Semivolatiles (water)	G(TC)	Store at 4° ± 2°C (in dark)	5 days from VTSR
Semivolatiles (soil/sediment)	G(TC)	Store at 4° ± 2°C (in dark)	10 days from VTSR[a]
Pesticides/PCBs (water)	G(TC)	Store at 4° ± 2°C (in dark)	5 days from VTSR[a]
Pesticides/PCBs (soil/sediment)	G(TC)	Store at 4° ± 2°C (in dark)	10 days from VTSR[a]

[a] Extract holding time is 40 days after extraction

P - plastic
G - glass
G(TC) - glass, TFE-lined cap
G(TS) - glass, TFE-lined septum

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[1] - USEPA Contract Laboratory Program; Statement of Work for Inorganics Analysis; Multi-media, Multi-concentration; SOW No. 3/90

USEPA Contract Laboratory Program; Statement of Work for Organics Analysis; Multi-media, Multi-concentration; SOW No. 3/90

Table 2
Summary of Required Sample Containers, Sample Volumes, Preservation Techniques And Storage Requirements
(from 40 CFR Part 136)

Parameter Name	Container[1]	Minimum Sample Volume[1,2]	Preservation[2,3]	Maximum Holding Time[4]
BACTERIAL TESTS				
Coliform, fecal and total	P, G (sterile)	200	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	6 hours
Fecal Streptococci	P, G (sterile)	200	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	6 hours
INORGANIC TESTS[7]				
Acidity	P, G	200	Cool, 4°C	14 days
Alkalinity	P, G	200	Cool, 4°C	14 days
Ammonia	P, G	200	Cool, 4°C, H_2SO_4 to pH < 2	28 days
Biochemical Oxygen Demand	P, G	1,000	Cool, 4°C	48 hours
Bromide	P, G	250	None	28 days
Chloride	P, G	50	None required	28 days
Chlorine, total residual	P, G	500	None Required	Analyze immediately
Color	P, G	500	Cool, 4°C	48 hours

Table 2
Summary of Required Sample Containers, Sample Volumes, Preservation Techniques And Storage Requirements
(from 40 CFR Part 136)

Parameter Name	Container[1]	Minimum Sample Volume (mL)	Preservation[2,3]	Maximum Holding Time[4]
Cyanide, total and amenable to chlorination	P, G	1,000	Cool, 4°C, H_2SO_4 to pH > 12, 0.6g ascorbic acid[5]	14 days[6]
Fluoride	P	1000	None Required	28 days
Hardness	P, G	200	HNO_3 or H_2SO_4 to pH < 2	6 months
Hydrogen ion (pH)	P, G	250	None Required	Analyze Immediately
3jeldahl and organic nitrogen	P, G	500	Cool, 4°C, H_2SO_4 to pH < 2	28 days
Chromium VI	P(A), G(A)	300	Cool, 4°C	24 hours
Mercury	P(A), G(A)	500	HNO_3 to pH < 2	28 days
Metals, except Chromium VI and Mercury	P(A), G(A)	500	HNO_3 to pH < 2	6 months
Nitrate	P, G	200	Cool, 4°C	48 hours
Nitrate-nitrite	P, G	200	Cool, H_2SO_4 to pH < 2	28 days
Nitrite	P, G	200	Cool, 4°C	48 hours

Table 2
Summary of Required Sample Containers, Sample Volumes, Preservation Techniques And Storage Requirements
(from 40 CFR Part 136)

Parameter Name	Container	Minimum Sample Size (ml)	Preservation[2,3]	Maximum Holding Time[4]
Oil and Grease	G, (wide mouth)	2000	Cool, 4°C, H_2SO_4 to pH < 2	28 days
Organic Carbon	P, G	100	Cool, 4°C, H_2SO_4 to pH < 2	28 days
Orthophosphate	P(A), G(A)	200	Filter Immediately, Cool 4°C	48 hours
Oxygen, dissolved (probe)	G Bottle and Top	300	None Required	Analyze Immediately
Winkler	G Bottle and Top	300	Fix on site and store in dark	8 hours
Phenols	G only	1000	Cool, 4°C, H_2SO_4 to pH < 2	28 days
Phosphorous, elemental	G	200	Cool, 4°C	48 hours
Phosphorous, total	P, G	200	Cool, 4°C, H_2SO_4 to pH < 2	28 days
Residue, total	P, G	200	Cool, 4°C	7 days
Residue, filterable (TDS)	P, G	200	Cool, 4°C	48 hours
Residue, nonfilterable (TSS)	P, G	200	Cool, 4°C	7 days
Residue, settleable	P, G	200	Cool, 4°C	48 hours

Table 2
Summary of Required Sample Containers, Sample Volumes, Preservation Techniques And Storage Requirements
(from 40 CFR Part 136)

Parameter Name	Container[1]	Minimum Sample Volume	Preservation[2,3]	Maximum Holding Time[4]
Residue, volatile	P, G	200	Cool, 4°C	7 days
Silica	P	500	Cool, 4°C	28 days
Specific Conductance	P, G	500	Cool, 4°C	28 days
Sulfate	P, G	50	Cool, 4°C	28 days
Sulfide	P, G	200	Cool, 4°C, add zinc acetate plus sodium hydroxide to pH > 9	7 days
Sulfite	P, G	100	None Required	Analyze Immediately
Surfactants	P, G	500	Cool, 4°C	48 hours
Temperature	P, G	250	None Required	Analyze
Turbidity	P, G	250	Cool, 4°C	48 hours

Table 2
Summary of Required Sample Containers, Sample Volumes, Preservation Techniques And Storage Requirements
(from 40 CFR Part 136)

Parameter Name	Container[1]	Minimum Sample Size (ml)	Preservation[2,3]	Maximum Holding Time[4]
ORGANIC TESTS[6]				
Purgeable Halocarbons	G, Tef.-lined septum	2X 40	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	14 days
Purgeable aromatic hydrocarbons	G, Tef.-lined septum	2X 40	Cool, 4°C, 0.008% $Na_2S_2O_3$[5], HCl to pH 2[9]	14 days
Acrolein and acrylonitrile	G, Tef.-lined septum	2X 40	Cool, 4°C, 0.008% $Na_2S_2O_3$[5], Adjust pH to 4-5[10]	14 days
Phenols[11]	G, Tef.-lined cap	2000	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
Benzidines[11]	G, Tef.-lined cap	2000	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	7 days until extraction[13]
Phthalate esters[11]	G, Tef.-lined cap	2000	Cool, 4°C	7 days until extraction; 40 days after extraction
Nitrosamines[12,14]	G, Tef.-lined cap	2000	Cool, 4°C, store in dark, 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
PCBs[11] acrylonitrile	G, Tef.-lined cap	2500	Cool, 4°C	7 days until extraction; 40 days after extraction

Table 2
Summary of Required Sample Containers, Sample Volumes, Preservation Techniques And Storage Requirements
(from 40 CFR Part 136)

Parameter Name	Container[1]	Minimum Sample Size (ml)	Preservation[2,3]	Maximum Holding Time[4]
Nitroaromatics and isophorone[11]	G, Tef.-lined cap	2000	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]. Store in dark	7 days until extraction; 40 days after extraction
Polynuclear aromatic hydrocarbons[11]	G, Tef.-lined cap	2000	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	7 days until extraction 40 days after extraction
Haloethers[11]	G, Tef.-lined cap	2000	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	7 days until extraction; 40 days after extraction
Chlorinated hydrocarbons[11]	G, Tef.-lined septum	2X40	Cool, 4°C	7 days until extraction; 40 days after extraction
PESTICIDES				
Pesticides[11]	G, Tef.-lined cap	1000	Cool, 4°C, pH 5-9[15]	7 days until extraction 40 days until extraction
RADIOLOGICAL TESTS				
Alpha, beta, radium	P, G	2000	HNO_3 to pH 2	6 months

1. Polyethylene (P) or Glass (G), G(A) or P(A) rinsed with 1:1 Nitric Acid

2. Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

3. When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.086% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.82 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

4. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time, and has received a variance from the Regional Administrator under 136.3(e). Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability. See 136.3(e) for details.

5. Should only be used in the presence of residual chlorine.

6. Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

7. Samples should be filtered immediately on-site before adding preservative for dissolved metals.

8. Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

9. Sample receiving no pH adjustment must be analyzed within 7 days of sampling.

10. The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

11. When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for seven days before extraction and for forth days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnotes (re: the requirement for thiosulfate reduction of residual chlorine), and footnotes 12 and 13 (re: the analysis of benzidine).

12. If 1,2-Diphenylhydrazine is likely to be present, adjust pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.

13. Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.

14. For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ and adjust pH to 7-10 with NaOH within 24 hours of sampling.

15. The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

SOP No: F.3

Title: Sample Logging and Record Keeping

Scope: This Standard Operating Procedure describes steps to be taken in the logging of samples and the records to be maintained by the Sample Control Location.

1.0 SAMPLE LOGGING PROCEDURES - INITIATION

1.1 All incoming samples must be inspected as outlined in SOP F.2, Sample Receipt, Inspection, Preservation and Storage Condition Requirements.

1.2 Individual incoming samples must have identification to differentiate between samples. Organize the samples into series according to the identification provided on the client sample submittal paperwork and check the actual samples received against the client paperwork. If there is an inconsistency between the sample labeling and the paperwork, the project manager will be notified and will contact the client. Discrepancies shall be noted in the Comments section of the Sample Receipt Checklist as described in SOP F.2.

1.3 Leave the samples in sequence until new GPL Laboratories sample labels are attached (See Section 2 of this SOP). The sample labels must be durable and indelible. Each sample container must be given a unique sample identification number provided by the LIMS. Samples requiring refrigeration should be placed on the "temporary holding" cart in the refrigerator (location A) until data entry procedures are complete and a permanent storage location is assigned. Note that samples requiring volatile analyses should be stored in the stand-alone refrigerators.

1.4 If a sample does not pass inspection, the Sample Coordinator should immediately notify the Sample Control Supervisor. Any discrepancies should be recorded in the Comments section of the Sample Receipt Checklist (Figure 1). The Sample Control supervisor will verify that the Project Manager/Client Services group is notified and provides specific instructions to the Sample Coordinator.

1.5 To facilitate the logging process, a Sample Receipt Checklist Form must be completed. If the project is governed by the EPA CLP program, then the CLP form DC-1(Figure 2)must be used, instead of the sample receipt checklist form.

1.6 A Sample Preservation Check Documentation Form (Figure 3) must also be completed if any samples containing acid preservative are received.

1.7 Attach the client paperwork to the sample receipt checklist, preservation check form and forward to the project manager group. After review by the project manager, 2nd approval, the paperwork must be returned to sample receiving.

2.0 SAMPLE LOGGING SUMMARY - DATA ENTRY

2.1 The Laboratory Information Management Systems (LIMS)

- Two LIMS programs are used for entering sample information into the LIMS system: The "Project Management" program and the "Sample Log-In" program.

- The Project Management/Client Services Group is primarily responsible for entering project information into the LIMS using the "Project Management" program.

- The Sample Control Group is primarily responsible for entering sample receipt information into the LIMS using the "Sample Log-In" program.

- The LIMS automatically assigns unique lab identifiers to the samples and produces forms used by managers to track every sample from log-in to invoicing.

2.1.1 Entering Project Information

Log on to Xenco

2.1.1.1 Create client information

Select Contacts & Companies icon at left of screen (icon has faces on it).
Select the Clients/Contacts tab.
Clear screen (brush icon at top of screen).
Select new client (green + icon at top of screen).
Check Company button.
Check Client? box at the right of the screen.
Create client code using company name and city: ie, CH2M_GAINESVILLE.
Fill in company name, address, phone number, fax number and e-mail, as applicable.
Select the zip code from the drop down menu. If the zip code is not on the list click on the Cities icon on the left of the screen. (It

is currently blank).
Type in the name of the city that you need in the indicated field.
From the drop down menu select the state and then Save (blue cassette icon at top of screen).
Click on the Zip Code button at the bottom of the screen.
Type in the new zip code in the indicated field.
From the drop down menu select the city and then Save.
The new zip code should now be in LIMS.
If the city name but not the correct zip code is already in LIMS click on the Zip Code icon on the left of the screen. (It is currently blank).
Type in the zip code in the indicated field.
From the drop down menu select the city and then Save.
The new zip code should now be in LIMS.
Close the Cities and Zip Code screens.
Go back to the Contacts and Companies screen and from the drop down menu select the city that you created.
When all information is entered Save the Contacts & Companies screen.
Successfully Saved message should appear.

2.1.1.2 Create contact information
Still in Contacts & Companies, select Contacts Tab.
Select Add Contact/Relationship icon (green + on right side of screen).
In Add New Contact screen, type in first name and last name of client contact in indicated boxes.
Click on Code box to automatically create name code.
Save screen. Successfully Saved message should appear.
Close Add New Contact screen.
Contact name should appear in Contact/Company column.
Select Contacts Info button on right, below the green + button.
Project Managers screen will appear with the new contact name showing.
Click on Name box at the bottom of the screen.
Use the drop down menu to select the company name to associate with the contact.
(Typing in the first few letters of the company name will take you to that part of the list.)
Highlight the company name and click OK or Enter.
The company should appear in the Name box.
Save screen and close the Project Managers screen.
The person should now be added as a contact for the company.
Close Contacts & Companies.

2 1.1.3 Create Project

Select Project & Quotes Management (P icon below W icon at left of screen).
Select the first tab, Project Specifications.
Clear screen (brush icon).
Select new project (green + icon).
Position cursor in Client box.
Click on the Client drop down menu and find the company that you created.
(Typing in the first few letters of the company name will take you to that part of the list.)
Highlight the company and click OK or Enter.
The company name should appear in the Client box.
Using the tab key or mouse, go to Project Name and type in the project name.
Go to Project ID and type in the ID (optional).
Click on Location box. This automatically brings up Gainesville as the default (lab location).
Click on Manager box and from the drop down menu highlight the contact that you created.
Click OK or Enter. The contact name should appear in the Manager Box.
Click on Director box and from the drop down menu highlight the contact.
Click OK or Enter. The contact name should appear in the Director Box.
Click on Lab PM box and from the drop down menu highlight the GPL project manager.
Click OK or Enter. The name should appear in the Lab PM Box.
Click on the Project Client box and from the drop down menu highlight the company name.
Click OK or Enter. The company name should appear in the Project Client Box.
Click on the Default TAT Box and from the drop down menu highlight the project TAT.
Click OK or Enter. The TAT should appear in the Default TAT Box.
Click on the Comments box and type in whatever info is needed to provide all analysts with the project requirements. At a minimum the type of data package and EDD requirements should be shown.
Save the screen.
Xenco will automatically assign the numbered Project Code at the top of the screen.

2.1.1.4 Create Methods

Still in Project & Quotes Management; select the second tab, Methods Requested.

The Method box at the left top of the screen will be highlighted.

In the Method box type in the method that you want to add to the project . SW846 methods all begin as SW###. MCAWW methods begin as E###. CLP methods begin with CLP_XXX.

The % sign can be used as a wild card if you don't know the exact method number.

After you have typed in a method number, double click on it. This will bring up all methods, which begin with the name that you typed in, in the Methods Selection list on the bottom left of the screen.

From Methods Selection click anywhere on the line of the method/matrix that you want to add to the project.

Click on the single right arrow [illegible] to the left of the list to move this method to the Methods for This Project list on the right.

Continue selecting methods until all of the required methods/matrices needed for the project are in the Methods For This Project list.

If a method is moved in the right in error, select the method and click the single left arrow to move it back.

Click on a selected method and arrow right until you get to the Prep 1 column.

Check that the correct prep method for each analysis is showing.

If you want to change the prep method, click on the box containing the prep code that you want to change and then click on the Refresh button at the top of the tab. This will bring up all associated prep methods in the box below the selected methods.

Click on the prep code that you want to use and then click on the large blue up arrow on the bottom left of the screen. This will move the selected prep up to the selected method.

You may save as you add each method or after you have all methods and prep codes selected

Xenco will bring up the message. Column 10 <QC Group {29}> at Row X is Required.

Click on the No box and the Successfully Saved message should come up.

The project should now contain all methods needed to log-in samples.

If you need to make a change after you have saved a method; select the box that needs to be revised, make the change and then highlight the entire row by clicking on the line number to the left of the line. Click Save. This will re-save only the line that had the change. If you want to delete an entire method/matrix, highlight the entire row by clicking on the line number on the left and then click on the Delete button at the top of the screen (red

X). Xenco will ask if you want to delete this information. Click Yes and the line will be removed. In order for a change or addition to work you may have to click anywhere in the section where you are making the change and click the Refresh button. You should then be able to make and save the change.

2.1.1.5 Select Method Analytes

Still in Project & Quotes Management; select the Analyses Requested tab.

All saved project methods will appear in the top box of the screen. Select the first method and click on the Refresh button at the top of the tab.

This will bring up all analytes associated with this method in the box on the bottom left.

Double click on the Description header bar and the analytes will sort in ascending or descending order, compounds beginning with numbers first.

Select each compound that should be reported, according specifications, and then click on the single right arrow to the left of the box, to move the analyte to the right box. If you want to select multiple analytes you can click on the first compound, hold down the left mouse button, drag down to highlight all analytes at the same time and then use the right arrow to move them all to the right.

If an analyte is selected in error hit the single left arrow to move it back to the left.

If you can't find a needed compound check the From Master box (*only "rom mas" shows) at the top left of the tab. This will refresh* the list of analytes to bring up every compound associated with the method. If you still can't find the compound that you need ask the System Admin to add it to the method/matrix.

You may Save as each compound is added or after all compounds have been selected and moved to the right.

The message X Rows Successfully saved will appear.

The project is now ready to use for logging in samples.

2.1.1.6 Making Changes

Projects may be updated/revised as follows:

Company address, phone numbers or e-mail can be revised at any time by doing the following:

Select Contacts & Companies.

Click the Enter Query icon at the top of the screen (red light turns green).

Check the Company box.

Type in the company code or company name. The % sign

can be used as a wild card.
Click the Search Query icon at the top of the screen (binoculars).
Companies matching the code or name will appear.
If more than one company is found click on the right arrow at the top left of the screen, next to the number 1, to move from one to the next until you find the company that you want.
Edit the company information as needed (except Code) and then Save.

Project name, Project ID, Manager, Director, Lab Project, Client, Default TA and Comments may be changed at any time by doing the following:

Select Project & Quotes Management.
Select the Project Specifications tab.
Click the Enter Query icon at the top of the screen (red light turns green).
Type in the project code number or use the drop down menu to select the client and type in any or all of the Project name.
The % sign can be used as a wild card.
Click the Search Query icon at the top of the screen (binoculars).
Company projects matching the code or name will appear.
If more than one company is found click on the right arrow at the top left of the screen, next to the number 1, to move from one to the next until you find the company that you want.
Type in the new information or use the drop down menus to make the changes and then Save.

List of analytes for each method may be changed at any time by doing the following:

Follow the steps above to find the correct company and project.
Select the Analytes Requested tab.
From the top box, select the method that you want to revise and click on the Refresh button to bring up the list of analytes.
For each analyte that you want to remove from the bottom right box; highlight the entire row by clicking on the line number on the left.
Click the Delete icon (red X) at the top of the screen.
Xenco will ask if you want to delete this information.
Click Yes and the analyte(s) will be removed.

To add analytes select them from the bottom left box and use the single right arrow to move them to the right box. Save.

Methods can be removed as long as they have never been used to log-in samples.

Follow the steps above to find the correct company and project.
Select the Analytes Requested tab first.
In the top box, select the method that you want to remove and click the Refresh button to bring up the list of analytes.
All analytes must be removed from the bottom box, by using the procedure in the previous paragraph, before the method can be deleted.
After all analytes have been deleted go back to the Methods tab.
You may have to refresh the methods list before you are able to delete it.
Highlight the entire row containing the method that you want to delete and click the Delete button (red X).
A prompt will ask if you want to delete this information.
Click Yes and the method will be removed.

2.1.2 Entering Sample Information

After logging in to a computer work station, there will be a configured menu item labeled "LIMS". A sub-menu item labeled "Sample Log-In" must be activated to load the Sample Log-In program. Either the program will prompt for a user ID and password, or else security information will be automatically supplied by the operating system.

Entering sample information is comprised of 4 parts: entering shipment (work order) record, entering sample records, entering sample bottle (fraction) records, and assigning analytical jobs to the samples.

The details of the procedure will depend on the software version being used, but the following are the essential basic steps for entering sample information.

- Enter the shipment (work order) information: project ID, sampling information, shipping information, date received, and turnaround time

- Add samples, entering sample information: client's sample ID, matrix, date of sampling.

- Add sample bottles (fractions), entering the storage location, and the container type.

- Assign analytical jobs to the samples by adding jobs and assigning the appropriate job codes.

2.1.3 Scheduling the Shipment (Work Order)

After entering all the information pertinent to a shipment (work order), the records must be inserted into the LIMS. Activate the function (available from the program's menu), for transferring the shipment (work order) into the LIMS. Once completed, the records are visible to all laboratory status checking and scheduling modules. New work orders are given status 25 when completed by sample management. Work orders are then checked by the project manager and given status 30 when completed.

2.1.4 Printing Forms

After the work order is complete, forms and sample labels should be printed. Labels contain the laboratory sample IDs for each sample as well as the tests to be performed on the sample.

Available forms are:

- Internal Chain of Custody (Figure 4).
- Work Order/Fraction Sheet, which lists all scheduled tests (Figure 5).
- Subcontracted Chain of Custody (Figure 6).

Forms may be printed individually, or using batches to redirect the form to it's proper destination within the facility.

2.1.5 Making Corrections

After a shipment has been logged in, it may still be modified (for example, a client may request additional analyses). Samples may be added or deleted, and jobs may be assigned or deleted after the shipment has been scheduled. Paperwork must be re-submitted after changes have been made to alert project managers and laboratory personnel.

A correction may be required using the Analysis Request Form (Figure 7).

2.2 Labeling the Samples

2.2.1 Obtain the labels from the label printer. Remove the labels from the wax paper backing and place on the corresponding samples. Verify that the correct label is being attached to the appropriate sample. Do not conceal any information that the client has provided on the sample.

2.3 pH Check for Preserved Samples

2.3.1 Chemical preservation of water samples is required by EPA for certain test parameters. SOP 7.2 "Sample Receipt, Inspection, Preservation, and Storage Condition Requirements" provides detailed information on this aspect of sample log-in. **Special Note:** Samples submitted from the Sample Management Office (SMO) under the Contract Laboratory Program (CLP) shall NOT be pH checked.

2.4 Organization of the Paperwork

2.4.1 Sample Receiving

- Internal Chain of Custody
- Subcontracted Chain of Custody
- Work Order(shipment)/Fraction (sample bottle)/Test Sheet
- Labels

2.4.2 Subcontractors

- Subcontracted Chain of Custody

2.4.3 Labs

- Work Order(shipment)/Fraction (sample bottle)/Test Sheet

2.5 Samples Requiring Immediate Analysis

2.5.1 The Sample Control Supervisor will notify the appropriate Project Manager when samples arrive that have a maximum holding time of 48 hours or less, or require immediate analysis.

2.6 Sample Receipt Notification

2.6.1 Some clients require notification that samples have been received. In such cases, the project manager supplies a copy of the COC, along with a copy of the sample receipt check list(figure 8).

3.0 SAMPLE STORAGE

3.1 All samples received for analyses are logged in according to the procedures detailed above and must be stored in such a manner as to maintain their integrity. Discrete sample locations based upon type of sample have been identified and are listed in SOP F.4, "Secure Sample Storage". Sample Control is maintained with restricted access at all times.

4.0 SAMPLE TRACKING

4.1 Samples may be distributed for analysis only after they have been logged into the LIMS system. Once a sample has been logged and stored, laboratory personnel must submit a request to Sample Control for the samples in accordance with the procedure described in SOP F.1, "Sample Chain-of-Custody". The analyst is ultimately responsible for the integrity of the sample while it is in his/her custody. Samples are to be returned to Sample Control immediately following analysis.

5.0 FINAL DISPOSITION OF SAMPLES

5.1 Commercial samples are kept for at least 90 days from the time the samples are received. After 90 days the samples are disposed of unless otherwise specified by the client. Disposal of all samples must be recorded in Sample Disposal Logbook.

5.2 Samples submitted for inorganic analysis under the Contract Laboratory Program will be retained for a period of 60 days after data submission. Extracts of samples submitted for organic analysis will be retained for a period of one year after data submission.

5.3 After the retention period, the samples are disposed of unless a written notice to the contrary is received. Ultimate disposition of all samples must be recorded in the Sample Disposal Logbook.

SOP D.1, Analytical Division Laboratory Waste Handling and Storage Procedures provides detailed guidance on the disposal of laboratory samples.

Figure 1
Sample Receipt Checklist

W.O. No: _____

Client Name: _____

Date Received: _____

Time Received: _____

Received By: _____

Carrier Name: _____

Prepared (Logged In) By: _____ / _____
Initials Date

Project: _____

Site: _____

VOA Holding Blank I.D. No: _____

	YES	NO
Airbill/Manifest Present?	___	___
No. _____		
Shipping Container in Good Condition?	___	___
Custody Seals Present on Shipping Container?	___	___
Condition: Broken _____		
Intact-not dated or signed _____		
Intact-dated and signed _____		
Usage of Tamper Evident Type	___	___
Chain-of-Custody Present?	___	___
Chain-of-Custody Agrees with Sample Labels?	___	___
Chain-of-Custody Signed?	___	___
Packing Present in Shipping Container?	___	___
Type of Packing _____		
Custody seals on Sample Bottles?	___	___
Condition: Good _____ Broken _____		
Total Number of Sample Bottles _____		
Total Number of Samples _____		
Samples Intact?	___	___
Sufficient Sample Volume for Indicated Test?	___	___

	YES	NO
Trip Blanks: No. of Sets _____	___	___
Field Blanks: No. of Sets _____	___	___
Equip. Blank: No. of Sets _____	___	___
Field Duplicate: No. of Sets _____	___	___
MS/MSD: No. of Sets _____	___	___
VOA Vials Have Zero Headspace?	___	___
Preservatives Added to Samples?	___	___
pH Check Required?	___	___
Performed By _____	___	___
Ice Present in Shipping Container?	___	___

Container #	Temp.	Container #	Temp.
_____	____	_____	____
_____	____	_____	____
_____	____	_____	____
_____	____	_____	____
_____	____	_____	____
_____	____	_____	____
_____	____	_____	____

Project Manager Contacted?
Name: _____
Date Contacted: _____

Any NO response must be detailed in the comments section below. If items are not applicable to particular samples or contracts, they should be marked N/A/

COMMENTS: _____

_____

_____

_____

Checklist Completed By: _____

Date: _____

Figure 2
Form DC-1

SAMPLE LOG-IN SHEET

Lab Name	Page __ of __
Received By (Print Name)	Log-in Date
Received By (Signature)	
Case Number	Sample Delivery Group No. / SAS Number

Remarks:

		EPA Sample #	Corresponding Sample Tag #	Assigned Lab #	Remarks: Condition of Sample Container
1. Custody Seal(s)	Present/Absent* Intact/Broken				
2. Custody Seal Nos.	_____ _____				
3. Chain-of-Custody Records	Present/Absent*				
4. Traffic Reports or Packing Lists	Present/Absent*				
5. Airbill	Airbill/Hand Carry Present/Absent*				
6. Airbill No.	_____ _____				
7. Sample Tags	Present/Absent*				
Sample Tag Numbers	List or Mat Listed on Chain-of-Custody				
8. Sample Condition	Intact/Broken*/ Leaking				
9. Cooler Temperature Indicator Bottle	Present/Absent*				
10. Cooler Temperature	_____				
11. Does information on custody records, Traffic Reports, and sample tags agree?	Yes/No*				
12. Date Received at Lab	_____				
13. Time Received	_____				
Sample Transfer					
Fraction	Fraction				
Area #	Area #				
By	By				
On	On				

* Contact SMO and attach record of resolution.

Reviewed By	Logbook No.
Date	Logbook Page No.

Figure 3
Sample Preservation Check Documentation Form

Work Order: ____________________

Parameter:	Metals	Phenol	TPH O&G	Classical Parameters	Cyanide	Sulfide	Radiology	Other
Preservative:	HN03	H2SO4	H2SO4	H2SO4	NaOH	NaOH	H2SO4	Preservations
pH Value	<2	<2	<2	<2	>12	>9	<2	
Client ID								

Sample Preservation Check Performed By: ____________________ **Date:** ____________________

Figure 4
GPL Internal C-O-C

Order : 211092 Received : 16-NOV-02 Received By : David CABILLAS

Samples : # Containers Keep For : 90 Days

Condition :

Samples Sign-Ou				Sample Return	
Fraction	Released By	Date / Time	Releases To	Date / Time	Deposition

Figure 5
GPL Work Order

GPL Laboratories

Work Order Approval

Page 1 of 1

Work Order #: 211092
GPL P Amy Edwards
Project #: 7833
Project Nam L14 25024

Comments: EXCEL EDD
GPL Level IV

Date Received Nov-16-2002
Fax Due Date:
HC Due Date:Dec-16-2002
EDD Due Date Dec-16-2002

APPROVED

Client: O'Brien & Gere
Address: 7001 North Atlantic Ave. Suite 202
Cape Canaveral, FL 32920
Contact: [illegible]
Phone: [illegible]
Fax: [illegible]
E-Mail:

Lab ID : 211092-001 Field ID : MCW02-5 Date Collected : 14-NOV-02

Method Name	tx	Cont	torage Loc	resev Class	AT	omments
Mercury by EPA 7470A	W	2	[illegible]	NCPH2	28D	
Residue, Filterable (TDS) by EPA 160.1	W	2	A-5B	COOL	28D	
Total Metals by EPA 6010B	W	2	A-5B	NCPH2	7D	

Lab ID : 211092-002 Field ID : MCW02-3 Date Collected : 14-NOV-02

Method Name	tx	Cont	torage Loc	resev Class	AT	omments
Mercury by EPA 7470A	W	2	A-5B	NCPH2	28D	
Residue, Filterable (TDS) by EPA 160.1	W	2	A-5B	COOL	28D	
Total Metals by EPA 6010B	W	2	A-5B	NCPH2	7D	

Lab ID : 211092-003 Field ID : MCW02-4 Date Collected : 14-NOV-02

Method Name	tx	Cont	torage Loc	resev Class	AT	omments
Mercury by EPA 7470A	W	2	A-5B	NCPH2	28D	
Residue, Filterable (TDS) by EPA 160.1	W	2	A-5B	COOL	28D	
Total Metals by EPA 6010B	W	2	A-5B	NCPH2	7D	

Lab ID : 211092-004 Field ID : MCWR02 Date Collected : 14-NOV-02

Method Name	tx	Cont	torage Loc	resev Class	AT	omments
Mercury by EPA 7470A	W	2	A-5B	NCPH2	28D	
Residue, Filterable (TDS) by EPA 160.1	W	2	A-5B	COOL	28D	
Total Metals by EPA 6010B	W	2	A-5B	NCPH2	7D	

Approved By: _____ Date and Time Approved : _____

Figure 6
Subcontracted C-O-C

Chain of Custody Form for
Subcontracted Analysis

GPL Laboratories, LLLP
202 Perry Parkway
Gaithersburg, MD 20877
(301) 926-6862
(301) 840-1269 (Fax)

GP W.O. No.: 211187

GP P.O. No.:

Samples Transferred To:

Attn:

Phone:

GP Lab Sample ID	Field Sample ID	Date Sampled	Time Sampled	Matrix	Analyses Requested	Method	Type of Container	Preservative
211187-002-023-1/1	E19-GW08-45-049	15-NOV-02	08:20	WATER	[illegible] METHOD 900.0	E900.0	1 L HDPE	NCPH2
211187-003-029-1/1	E19-GW08-45-050	15-NOV-02	08:20	WATER	[illegible]	E900.0	500 ML HDPE	NCPH2

Carrier:

Airbill No.:

Report Due On:

Send Report Attn:

Perform Q.C. on Sample:

Condition Upon Receipt:

Comments:

Samples Relinquished By: Date: Time:

Samples Received By: Time:

Figure 7
Analysis Request Form

ANALYSIS REQUEST FORM

DATE REQUESTED

COMPLETED BY

WORK ORDER #	SAMPLE ID	MATRIX	DATE SAMPLED	DATE EXTRACTION	ADDITIONAL ANALYSIS	DUE DATE

SOP No: F.4

Title: Secure Sample Storage

Scope: This Standard Operating Procedure describes the procedures used to maintain secure storage conditions for laboratory samples and extracts.

1.0 SAMPLE SECURITY

1.1 Sample Control

The Sample Control facility is the area where samples are received, logged-in, and stored. It is maintained as a controlled limited access area. It is locked at all times and only Sample Control personnel and their supervisors have keys to the area. When samples are needed by the laboratories, a sample request is made and Sample Control personnel retrieve the samples. Samples are transferred to laboratory personnel, with proper chain-of-custody documentation maintained by Sample Control personnel.

1.2 Laboratories

Some analyses result in extracts which may be stored prior to instrument analysis. These extracts are maintained under secure conditions in locked laboratories prior to analysis and, where applicable, for storage of the extracts.

2.0 SAMPLE CONTROL STORAGE LOCATIONS

SOP F.2, " Sample Receipt, Inspection, Preservation and Storage Condition Requirements " includes information on the storage conditions required for samples analyzed by the laboratory.

Sample Control maintains storage areas for both room temperature and refrigerated storage of samples. Each individual storage location (refrigerator or storage cabinet) has a unique identifier code. Within each unit each shelf is also identified with a tag for further traceability of storage location. Each individual location designation, location description and the sample assignments are detailed below.

Location Designation	Location Description	Sample Assignment
A-1 to A-8 A-13 to A-18	Walk-in refrigerator, Shelving Units	All samples which require refrigeration except VOA samples
A-19	Reach-in refrigerator	VOA soils only
A1	Reach-in refrigerator	VOA water only
A2	Reach-in refrigerator	VOA water only
A3	Reach-in refrigerator	CLP water/soil samples (VOA)
A9	Reach-in refrigerator	All samples which require refrigeration except VOA samples
A10	Reach-in refrigerator	All samples which require refrigeration except VOA samples
A11	Reach-in refrigerator	All samples which require refrigeration except VOA samples
A12	Reach-in refrigerator	All samples which require refrigeration except VOA samples
4	Room Temperature Cabinet	All PE samples which require room temperature storage
5	Room Temperature Cabinet	Aqueous metals samples which require room temperature storage
6	Room Temperature Cabinet	Aqueous metals samples which require room temperature storage
7	Room Temperature Cabinet	Extra cabinet

8	Room Temperature Cabinet	PCB samples only
B	Walk-in #2	All samples which require refrigeration except VOA samples
9	Room Temperature Cabinet	TCLP extract storage
10	Room Temperature Cabinet	TCLP extract storage

In order to monitor volatile storage area for cross contamination, the laboratory keeps at least one storage blank in each volatile storage area at all times. The storage blank from each storage area must be analyzed. The storage blank data must be maintained in VOA section. If storage blank analyses provides evidence of cross contamination during storage, corrective action must be taken.

3.0 SAMPLE EXTRACT STORAGE

3.1 Organic Sample Extract Storage

Organic sample extracts are prepared in the Organic Extraction Laboratory. They are stored in designated refrigerators in the GC-GC/MS laboratory prior to analysis. One refrigerator is designated for GC analysis extracts only while another is identified for GC/MS extracts only. This laboratory complex is maintained secure by use of cipher locks on the doors. Only employees and supervisors who work in the area are provided with the combination needed to enter. Transfer of the extracts into the designated refrigerators is documented on the Sample Extract Storage Log (Figure 1) Sheet for each refrigerator. Organic sample extracts are received, signed by and remains in the custody of the organic section supervisors.

3.2 Metals Digestate Storage

Samples which require metal analysis require a digestion process. The resulting digestates are transferred to the Metals Laboratory for storage. The sample digestate bottles are placed in plastic trays labeled with the sample groups Work Order number and are stored on designated shelving units within the High Concentration Laboratory portion of the Metals Laboratory complex. The Metals Laboratory is maintained as a secure lab through the use of cipher locks. Only personnel who work in the area are given the access code. Metals digestates are received, signed by and remains in the custody of the metals supervisor.

3.3 Wet Lab Digestate Storage

Digestates produced in the Wet Lab are stored in a designated refrigerator located within Sample Control. Wet chemistry digestates are received, signed by and remains in the custody of the section supervisor.

3.4 VOA Samples

VOA samples are received and signed by the VOA section supervisor and stored in the refrigerator located in VOA lab prior and after analysis, until returned to the sample management office. Samples remain in the custody of the VOA section supervisor at all times and the supervisor assigns the samples to designated analysts. The VOA lab is maintained secure by the use of siphon lock on all exit doors. Only the designated staff have access to the VOA lab.

4.0 SAMPLE STORAGE CONDITIONS

4.1 Room Temperature

Room temperature storage cabinets are maintained with the [illegible] samples are being stored or retrieved. Room temperature is monitored and recorded by Sample Control personnel daily. Excesses in temperature are avoided since the area is heated and air conditioned.

4.2 Refrigerated Storage

Refrigerator temperatures are monitored daily and recorded. The required temperature is 4 ± 2°C. If temperatures exceed the range, the supervisor of that section is notified, who then contacts the building maintenance supervisor. If repair is required to a unit, the repair shall be documented. Please see SOP G.6, Temperature Monitoring for details.

Figure 1

GPL Laboratories, LLLP

Documnet Control No: GP_G_028

SAMPLE EXTRACTION STORAGE AND CHAIN OF CUSTODY
BC REFRIG-6

Project Number	GPL Work Orders	Number of Samples	Method Parameter	Relapsed By	Released To	Released Date	Sample Custody of	Date	Returned By	Date Returned

SOP No: F.5

Title: Sample Container Quality Assurance Program

Scope: This Standard Operating Procedure details the Quality Assurance Program for providing sample containers for use in the collection of analytical samples.

1.0 PURPOSE

1.1 The purpose of this procedure is to define a program whereby the laboratory provides fully traceable, properly documented sampling bottles of known quality to field sampling operations.

2.0 EQUIPMENT AND SUPPLIES

- I Chem level 300- pre-cleaned and certified
- 1:1 HNO_3 - prepared by adding equal quantities of metals grade nitric acid to laboratory ultra pure water
- 1:1 $H2SO_4$ - prepared by adding equal quantities of metals grade sulfuric acid to laboratory ultrapure water
- 1:1 HCL - prepared by adding equal quantities of metals grade hydrochloric acid to laboratory ultra pure water
- 5N NaOH - purchased as 5N solution
- Hexane 2ml (pesticide grade)
- Sodium thiosulfate 0.008% in water
- 2N-zinc acetate
- Ascorbic acid

CAUTION: Extreme care must be used when preparing solutions. Each solution must be prepared in a hood and the preparation container must be cooled to prevent breakage. Always add acid to water when preparing solutions.

Personnel Safety Equipment:

- Safety glasses/goggles
- Rubber gloves
- Lab coat
- Lab apron

3.0 SAMPLE CONTAINER DOCUMENTATION

Sample containers supplied by GPL Laboratories for collection of samples in the field must be of the right type, appropriately prepared, and properly documented.

3.1 Documentation of Sample Container Receipt

3.1.1 After sample containers have been checked through the Sample Management group, the Sample Management group supervisor inspects the arrived boxes and determines the condition of sample containers received and places them in container storage room.

3.1.2 Class I sample containers are pre-cleaned, tested and come with Certificates of Analysis. Lot numbers of the containers are noted on the bottle request sheets and Certificates of Analysis are gathered and placed in the Certificate of Analysis files. Lot numbers are not assigned by the lab since they are already assigned by the supplier. Class I sample containers do not require testing and are placed on the designated shelves for immediate use.

3.2 Sample Container Storage Area Monitoring

3.2.1 It is required that sample containers be stored in a contaminant-free area to prevent container from being contaminated with potential analytes. To meet this requirement the storage area shall be continuously monitored for volatile contaminants.

3.2.3 A certified 40mL VOA vial shall be filled with laboratory ultra pure water and placed in the storage area. The vial shall be changed bimonthly by volatile staff. The vial which was removed shall be analyzed for volatile organics. When the data is reviewed by the Lab Director it should be noted that any peaks represent contamination. Contaminants shall be identified, possible sources investigated and recommendations made to management on how to reduce the problem.

3.3 Sample Container Storage Location

Sample containers are stored in the office in hallway by the computer room.

4.0 SAMPLE CONTAINER SPECIFICATIONS

4.1 The containers required, whether plastic or glass, must be of good quality, must be used with teflon liners were required, must seal completely, and must not in any way compromise the integrity of the sample. Sample containers must always be new and shall be discarded after use.

4.2 Plastic bottles shall be made of High Density Polyethylene (HDPE) with secure fitting polyethylene or polypropylene caps. Plastic containers are made of polyethylene (HDPE) with a polypropylene cap. All caps shall have a polyethylene coated liner. Glass bottles shall be made of flint glass (clear) or amber glass as needed and shall have teflon cap liners supplied.

5.0 SAMPLE CONTAINER PREPARATION

5.1 Client orders for bottle requests are completed in the sample receiving area as per the request of the project manager. A bottle preparation form must be completed by the project manager (see attached). The document specifies the client requirements of the bottle type according to the analyses. The information includes the bottle size/type, required preservative, acid lot #, client information, bottle QC and other pertinent information. Bottles are prepared according to the information recorded on the preparation sheet and are packed in coolers for shipment using either bubblewrap or vermiculite (bubblewrap unless otherwise specified). Coolers will also contain a chain-of-custody form, custody seals, ice packs and trip blanks, when specified.

5.2 The following information details the preservation procedure for the listed methods:

- Metals analyses in water:
  - 500ml plastic add 2ml of 1:1 HN03
  - 1 liter plastic add 4ml of 1:1 HN03
- Oil and Grease or TPH (418.1) analyses in water:
  - 1 liter amber glass add 2ml of 1:1 H_2SO_4
- Cyanide analyses in water:
  - 1 liter plastic add 2ml of 5N NaOH

- BNA, Pesticide, PCBs or Herbicides in Water:
  - 1 liter amber glass - unpreserved, unless specified by client
- Volatile analysis in water:
  - 2x40ml VOA vials with 1ml of 1:1 HCL or unpreserved

The addition of preservatives is not necessary for bottles designated to contain soil samples.

To prepare a sample trip blank, completely (zero-headspace) fill a VOA vial with ultra pure water. HCL is used as a preservative only when the other VOA vials are preserved.

5.3 Documentation

- Lot numbers of both acids and bottles are recorded on the bottle, with the bottle preparation form. A copy of the form is submitted to the client and a copy is maintained in the GPL client files in the sample receiving department.

Table 1

SAMPLE CONTAINER
SPECIFICATIONS

Container Type	Specifications
A	Container: 80 oz. amber glass, ring handle bottle/jug, 38mm neck finish. Closure: blue phenolic, baked polyethylene cap, 38-430 size; .015 mm teflon liner.
B	Container: 40mL glass vial, 24mm neck finish. Closure: blue phenolic, open-top, screw cap, 15cm opening, 24-400 size. Septum: 22mm disc of .005 inch teflon bonded to .120 inch silicon for total thickness of .125 inch.
C	Container: 1 liter high-density polyethylene, cylinder-round bottle, 28mm neck finish. Closure: white polyethylene, blue ribbed, 28-410 size; F217 polyethylene liner.
D	Container: 120mL wide mouth, glass vial, 48mm neck finish. Closure: blue polypropylene cap, 48-400 size; .015mm teflon liner.
E	Container: 16 oz. tall, wide mouth, straight-sided, flint glass jar, 63mm neck finish. Closure: blue phenolic, baked polyethylene cap, 63-400 size; 0.15 mm teflon liner.
F	Container: 8 oz. short, wide mouth, straight-sided, flint glass jar, 70mm neck finish. Closure: blue phenolic, baked polyethylene cap, 58-400 size; .030 mm teflon liner.
G	Container: 4 oz. tall, wide mouth, straight-sided, flint glass jar, 48mm neck finish. Closure: blue phenolic, baked polyethylene cap, 48-400 size; .015 mm teflon liner.
H	Container: 1 liter amber, Boston round, glass bottle, 33mm pour-out neck finish. Closure: blue phenolic, baked polyethylene cap, 33-430 size; .015 mm teflon liner.

Table 1

SAMPLE CONTAINER
SPECIFICATIONS
(Continued)

Container Type	Specifications
J	Container: 32 oz. tall, wide mouth, straight-sided, flint glass jar, 89mm neck finish. Closure: blue phenolic, baked polyethylene cap; 38-400 size; .015mm teflon liner.
K	Container: 4 liter amber glass, ring handle bottle/jug, 38mm neck finish. Closure: blue phenolic, baked polyethylene cap, 38-430 size; .015mm teflon liner.
L	Container: 500mL high-density polyethylene, cylinder-round bottle, 28mm neck finish. Closure: white polypropylene cap; blue ribbed, 28-410 size; F217 polyethylene liner.

Table 2

BOTTLE PREPARATION REQUEST

Project Name/No: _____ Date/Time of Request: _____ Requested By: _____

Date Required by Client: _____ Method of Shipment: _____

Shipment Address: _____

No. of Bottles	Bottle Size/Type	Required Preservative	Add Lot #	Analysis

Other Requirements: *All bottles are EPA Certified Clean Level I*

Bottle Labels:	Blank _____	Labeled as shown above _____		Not Required _____	
Coolers:	Yes _____	Amt. Required _____		Not Required _____	
Ice Packs:	Yes _____	Amt. Required _____		Not Required _____	
Chain of Custody Forms:	Yes _____	Amt. Required _____		Not Required _____	
Custody Seals:	Yes _____	Amt. Required _____		Not Required _____	
VOA Trip Blanks (2 vials/set with HCl)	Yes _____	No. of Sets Required _____		Not Required _____	
Temperature Blanks:	Yes _____	Amt. Required _____		Not Required _____	

Comments: _____

EPA Level I bottles Lot Number: _____

Date Bottles Prepared: _____ Prepared By: _____

Total No: Coolers _____ Boxes _____ Ice Packs: _____

Date Shipped: _____ Shipped By: _____ Method of Shipment/Tracking No: _____

SOP No: M.7

Title: Method 5035 – Closed System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples

1.0 SCOPE AND APPLICATION

1.1 This method describes a closed-system purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in soil materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. These procedures are based in conjunction with any appropriate determinative chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

2.0 SUMMARY OF METHOD

2.1 Volatile organic compounds – generally applicable to and soils and other solid samples with VOC concentrations in the range of 0.5 to 200µg/kg.

Volatile organic compounds (VOCs) are determined either by collecting an approximately 5g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate preservative solution, or see Section 6.4.3. The vial is sealed and shipped to the laboratory. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration soil method – generally applicable to soils and other solid samples with VOC concentrations greater than 200µg/kg.

The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/EC, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to this solution, then purged using Method 5030 and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5g sample in a pre-weighed vial with a plunger-sealed septum that contains 5mL of a water-miscible solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, and an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

2.3 High concentration oil/waste method – generally applicable to oily samples with VOC concentrations greater than 200µg/kg that can be diluted in a water-miscible solvent.

3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and acetone) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers handling previously exposed to methylene chloride fumes during collection of liquid extraction procedures can contribute to sample contamination. Trip blanks and other organic solvents in the laboratory where volatile organics are analyzed have also been shown to lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Sample Containers

The purge-and-trap system employed at GPL requires 40ml clear screw cap vials with Teflon-faced low bleed septa.

4.2 Purge-and-Trap System

The purge-and-trap system consists of a Tekmar LSC-2000 concentrator equipped with an Archon autosampler that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph.

4.2.1 The purging device is capable of accepting 40ml vial that contains a 5g soil sample plus a magnetic stirring bar and 10mL of water. The device is capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device is also capable of introducing at least 5mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors.

It is also capable of agitating the sealed sample during purging (using a magnetic stirring bar added to the vial prior to sample collection). The analytes being purged is quantitatively transferred to an absorber trap.

4.2.1.1 The trap used for this method is 25cm long, with an inside diameter of 0.105 inches, made of charcoal and marketed under VOCARB 3000.

4.2.2 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

4.3 Syringe and Syringe Valves

4.3.1 25mL glass hypodermic syringes with Luer-lok (or equivalent). Other sizes are acceptable depending on sample volume used).

4.3.2 2-way syringe valves with Luer ends.

4.3.3 25µL micro syringe with a 2 inch x 0.006 inch ID, 22 gauge needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes 10, 100µL.

4.3.5 Syringes 0.5, 1.0 and 5mL gas tight with shut-off valve.

4.4 Miscellaneous

4.4.1 Glass vials

4.4.1.1 40mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

4.4.2 Top-loading balance – Capable of accurately weighing to 0.01g.

4.4.3 Glass scintillation vials – 20mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

4.4.4 Volumetric flasks – Class A, 10mL and 100mL, with ground-glass stoppers.

4.4.5 2mL glass vials, for GC autosampler – used for oily waste samples extracted with methanol of PEG.

4.4.6 Spatula, stainless steel – narrow enough to fit into a sample vial.

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4.4.7 Disposable Pasteur pipettes.

4.4.8 Magnetic stirring bars – PTFE-coated. Stirring bars are reused, provided that they are thoroughly cleaned between uses.

5.0 REAGENTS

5.1 Organic-free reagent water – all references to water in this method refer to organic-free reagent water, as defined in Chapter One of SW846.

5.2 Methanol, CH_3OH – purge-and-trap quality or equivalent. Stage away from other solvents.

5.3 Low concentration sample preservative.

5.3.1 Sodium bisulfate, $NaHSO_4$ – ACS reagent grade or equivalent.

5.3.2 The preservative should be added to the vial prior to shipping to the field and must be present in the vial prior to adding the sample.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Preparation of sample vials.

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and delivered to the field location. Gloves should be worn during the preparation steps.

6.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in this SOP.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial.

6.1.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2g of preservative for each 1g of sample. Enough sodium bisulfate should be present to ensure a sample pH of ≤2.

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6.1.1.3 Add 5mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes. If an efferescing matrix is encountered samples should be handled according to the procedure note in Section 6.2.1.2.

6.1.1.4 Seal the vial with the screw-cap and septum seal.

6.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.1.6 Weigh the prepared vial to the nearest 0.01g, record the tare weight, and write it on the label.

6.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous phase, they will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vial after the sample has been added to the vial. These standards should be introduced back in the laboratory automatically by the sample introduction system prior to analysis.

6.1.2 High concentration soil samples collected without a preservative.

When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 60mL glass vials with septum seals (see Sec. 4.4).

6.1.3 High concentration soil samples collected and preserved in the field.

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030.

6.1.3.1 Add 10mL of methanol to each vial.

6.1.3.2 Seal the vial with the screw-cap and septum seal.

6.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.3.4 Weigh the prepared vial to the nearest 0.01g, record the weight, and write it on the label. Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01g) should not be used for sample collection.

6.1.3.5 Surrogates, internal standards and matrix spikes (if applicable) should be added to the vial containing the soil sample after it is returned to the laboratory and prior to analysis.

6.2 Sample Collection

This section is not applicable to the laboratory operation, [illegible] with sample collection would help the analyst with proper implementation of Method 5035.

Collect the sample according to the procedures outlined in the sampling plan. A[illegible] with any sampling procedure for volatiles [illegible] be taken to minimize disturbance of the sample in order to maintain the shapes of the soil components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the Encore Sampler, the Purge-and-Trap Soil Sampler™, and a cut plastic syringe. [illegible] handling the tared sample vials.

6.2.1 Low concentration samples

6.2.1.1 Using an appropriate sample collection device, collect approximately 5g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.1.2 Using the sample collection device, add about 5g (2-3cm) of soil to the sample vial containing the preservative solution. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

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

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levels of carbonates, a test sample should be collected, added to a vial, and a checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect low concentration samples in vials that do not contain the preservative solution. Add 5ml of reagent grade organic free water to the sample vial. Then samples should be shipped to the lab within 48 hours of collection while kept at 4° ± 2°. Upon sample receipt, the lab must freeze the samples at temperatures below minus 10°C for up to a period of 12 days. Overall sample analysis should be performed within 14 days from the collection date. Sample vials must be kept filled in the freezer to minimize the circumferential pressure of water expansion on the glass vial.

6.2.1.3 When practical, use a portable balance to weigh the sample vial containing the sample to ensure that 5.0 ± 0.5g of sample is added. The balance should be calibrated in the field using appropriate weights or the sample container equivalent (SOP 4.5.5). Record the weight of the filled vial containing the sample to the nearest 0.01g.

6.2.1.4 Alternatively, collect soil trial samples with plastic syringes. Weigh the trial sample and determine length of the soil column in the syringe. Use this to calculate and determine the length of soil in the syringe that collects 5.0 ± 0.5g. Discard each trial sample.

6.2.1.5 As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for re-analysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

6.2.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, dry weight determination, and high concentration analysis (if necessary). This third aliquot may be collected in a 60mL glass vial or a third 40mL soil sample vial. However, this third vial must not contain the sample preservative solution, as an aliquot will be used to determine dry weight. If high concentration samples are collected in vials containing methanol, then two additional aliquots should be collected, one for high concentration analysis collected in a vial containing methanol, and another for the dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

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6.2.1.7 If samples are known or expected to contain target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1-2g instead of the 5g collected in Sec. 6.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5g analysis.

6.2.1.8 The EnCore™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore™ device may be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, ideally within 48 hours. Samples should be taken in duplicate (per [illegible]) and shipped to the lab immediately after collection. The lab should transfer the EnCore™ cartridges to clean 40ml vials and add aliquots of water to the vials and methanol to the third vial following the procedure in Section 6[illegible].

6.2.1.9 The collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (Sec. 12.2[illegible]).

6.2.2 [illegible] samples preserved in the field.

6.2.2.1 The collection of soil samples in vials that contain methanol has been [illegible] by [illegible] a combined preservation and extraction [illegible]. However, this procedure is not appropriate for use with the [illegible] soil procedure described in this method.

6.2.2.1.1 When samples are known to contain volatiles at concentrations high enough that the dilution factor will not preclude obtaining results within the calibration range of the appropriate determinative method, a sample may be collected and immediately placed in a sample vial containing purge-and-trap grade methanol.

6.2.2.2 Using an appropriate sample collection device, collect approximately 5g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

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6.2.2.3 Using the sample collection device, add about 5g (2-3cm) of soil to the vial containing 10mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

6.2.2.4 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01g.

6.2.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil plug in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5g. Discard each trial sample.

6.2.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

6.2.2.7 The collection of at least one additional sample aliquot is required for the determination of dry weight, as described in Sec. 11.2.1.6. Samples collected in methanol should be shipped as described in Sec. 6.3, and must be clearly labeled as containing methanol, so that the samples are not analyzed using the closed-system purge-and-trap equipment described in this procedure.

6.2.3 High concentration soil sample not preserved in the field.

The collection of high concentration soil samples that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 6.2.1 and 6.2.2, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for dry weight determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

6.3 Sample handling and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan.

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6.4 Sample Storage

6.4.1 Once in the laboratory, store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 All samples should be analyzed within 14 days from collection date.

6.4.3 Sample collected in EnCore™ cartridges should be analyzed within [illegible] hours from collection or transferred to 40ml VOA vials preserved [illegible] analyzed within 12 days. Refer to Section 6.2.1.2.

6.4.4 When the low concentration samples are strongly alkaline or [illegible] calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to [illegible]. Therefore, when low concentration soil samples are sampled and [illegible] suspected to be strongly alkaline or highly calcareous, additional [illegible] may be required to preserve the samples. Such supplemental [illegible] of larger amounts of the sodium bisulfate preservative may be required [illegible] samples, storage of low concentration samples at [illegible] (taking care not to fill the vials so full that the addition of the water [illegible] the vial breaks the vial), or shorter [illegible] holding time for low concentration [illegible] are employed, they should be [illegible] and QA project plans and distributed to [illegible] personnel. See Sec. 6.2.1.2 for additional information.

[illegible]

[illegible] procedures for the low concentration soil method and the high concentration soil method. High concentration samples are to be introduced into the [illegible] system using Method 5030.

[illegible] low concentration soil method (approximate concentration range of 0.5 to [illegible]200µg/kg – the concentration range is dependent upon the determinative method and the sensitivity of each analyte).

7.1.1 Initial Calibration

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in the related GC or GCMS method SOPs. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed.

7.1.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

7.1.1.2 Before initial use, a VOCARB 3000 trap should be conditioned 2 hours at 245°C by backflushing with an inert gas flow of at least 20mL/minute. Prior to daily use, the trap should be conditioned for 10 minutes at 245°C with backflushing.

7.1.1.3 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5mL of water to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes prior to commencing the purge process, or as recommended by the instrument manufacturer.

7.1.1.4 Prepare a minimum of five initial calibration standards containing all the analytes of interest, surrogates, as described in the Method SOP, and following the instrument manufacturer's instructions. The calibration standards are prepared in organic-free reagent water. The volume of organic-free reagent water used for preparation of the standards is the same as the volume used for sample analysis (5mL) to be equal before shipping it to the laboratory, the organic-free reagent water added by the instrument). The calibration standards should also contain approximately the same amount of the sodium bisulfate preservative as the sample (7g, 1g). The presence of the preservative will affect the purging efficiencies of the analytes. The internal standard solution must be added automatically, by the instrument, in the same manner as used for the samples. Place the soil vial containing the solution in the instrument carousel. In order to calibrate the surrogates using standards at five concentrations, it is necessary to disable the automatic addition of surrogates to each vial containing a calibration standard. Prior to purging, heat the sample vial to 40°C for 1.5 minutes.

7.1.2 Continuing Calibration

Refer to Method SOPs for details on continuing calibration. A single standard near the mid-point of calibration range is used for verification. This standard should also contain approximately 1g of sodium bisulfate.

7.1.3. Method Detection Limits

Method detection limits for this method are listed in the GPL Laboratory Method Detection Limit and Reporting Limit official book.

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7.1.4 Method Performance

The MDL concentrations listed in the GPL MDL book are generally obtained using organic-free reagent water. Results were also obtained by extracting seven spiked replicates the same way as the samples and analyzing them. MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. Precision and accuracy studies are performed once a year at a minimum. Single operator precision, overall precision and method accuracy were found to be directly related to the concentration of the parameter.

7.1.5 Sample purge-and-trap

This method is designed for a 5g sample size, but smaller sample sizes may be used. The soil vial is hermetically sealed at the sampling site and MUST remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.01g, even if the sample weight was determined in the field and recorded this weight. This second weighing provides a check of the field sampling procedures and provides additional assurance that the reported sample weight is accurate. Data users should be advised on significant differences between the field and laboratory weights.

7.1.5.1 Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel.

7.1.5.2 Without disturbing the hermetic seal on the sample vial, add 5mL of organic-free reagent water, the internal standards, and the surrogate compounds. This is carried out using the automated sampler. Other volumes of organic-free reagent water may be used, however, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water. Prior to purging, heat the sample vial to 40°C for 1.5 minutes.

7.1.5.3 For the sample selected for matrix spiking, add the matrix spiking solution described I Sec. 5.0 of Method 5000, either manually, or automatically. The concentration of the spiking solution and the amount added should be established as described in the related SOP.

7.1.5.4 Purge the sample with helium at a flow rate of up to 40mL/minute (the flow rate may vary from 20 to 40mL/min, depending on the target analyte group) for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap.

7.1.6 Sample Desorption

After the 11 minute purge, place the purge-and-trap system in the desorption mode and preheat the trap to 245°C without a flow of desorption gas. Start the flow of desorption gas at 10mL/minute for about two minutes. Begin the temperature program of the gas chromatograph and start data acquisition.

7.1.7 Trap Reconditioning

After desorbing the sample for 4 minutes, condition the trap by returning the purge-and-trap system to the purge mode and raising the trap temperature at 245°C. After approximately 8 minutes, turn off the trap heater and halt the purge gas flow through the trap. When the trap is cool, the next sample can be analyzed.

7.1.8 Data Interpretation

Perform qualitative and quantitative analysis following the guidance given in the qualitative and quantitative methods and method SOPs. If the concentration of any target analyte exceeds the calibration range of the instrument, it will be necessary to reanalyze the sample by the high concentration method. Such re-analyses need only address those analytes for which the concentration exceeded the calibration range of the low concentration method. Alternatively, if a sample aliquot of 1-2g was also collected (see Section 7.2.1.7), it may be practical to analyze that aliquot for the analytes that exceeded the instrument calibration range in the 5g analysis.

7.2 High concentration method for soil samples with concentrations generally greater than 200µg/kg.

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility in a water-miscible solvent. An aliquot of the extract is added to organic-free reagent water containing surrogates and, if applicable, internal and matrix spiking standards, purged according to Method 5030, and analyzed by an appropriate determinative method.

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The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.2.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 7.2.4.

7.2.1 When the high concentration sample is not preserved in the field, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Whenever practical, mix the contents of the sample container by shaking or other mechanical means without opening the vial. When shaking is not practical, quickly mix the contents of the vial with a narrow metal spatula and immediately reseal the vial.

7.2.2 For soil and solid waste samples that are soluble in methanol, add 9.0mL of methanol and 1.0mL of the surrogate spiking solution to a tared 2mL vial. Using a top-loading balance, weigh 5g (wet weight) of sample into the vial. Quickly cap the vial and reweigh the vial. Record the weight to 0.1g. Shake the vial for 2 min. If the sample was not soluble in methanol, but was soluble in PEG, employ the same procedure described above, but use 9.0mL of PEG in place of the methanol. Proceed with Sec. 7.2.5.

7.2.3 For soil and solid waste samples that were collected in methanol or PEG (see Sec. 7.2.2), weigh the vial to 0.1g. Check on the weight recorded in the field for the surrogate spiking solution to the vial by injecting it through the septum and shake the vial as described above, and proceed with Sec. 7.2.5.

7.2.4 Transfer approximately 1mL of the extract from either Sec. 7.3.3 or 7.3.4 into a GC vial for storage, using a disposable pipette, and seal the vial. The remainder of the extract may be discarded. Add approximately 1mL of methanol or PEG to a separate GC vial for use as the method blank for each set of samples extracted with the same solvent.

7.2.5 The extracts must be stored at 4°C in the dark, prior to analysis. Add an appropriate aliquot of the extract (see Table 2) to 5.0mL of organic-free reagent water and analyze by Method 5030 in conjunction with the appropriate determinative method.

7.2.6 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the procedure in Sec. 7.3, after the sample extract has been transferred to a GC vial and the vial sealed.

7.3 Determination of % Dry Weight

If results are to be reported on a dry weight basis, it is necessary to determine the dry weight of the sample.

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NOTE: It is highly recommended that the dry weight determination only be made after the analyst has determined that no sample aliquots will be taken from the 60mL vial for high concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere. There is no holding time associated with the dry weight determination. Thus, this determination can be made any time prior to reporting the sample results, as long as the vial containing the additional sample has remained sealed and properly stored.

7.3.1 Weigh 5-10g of the sample from the 60mL VOA vial into a tared crucible.

7.3.2 Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

8.0 SAFETY

8.1 Always wear safety glasses or a shield for eye protection, gloves and lab coat.

8.2 Observe proper [illegible] reagents and chemicals. Preparation of samples [illegible] should be handled under the hood.

8.3 A [illegible] sheet is available to all personnel involved in these analyses.

9.0 WASTE MANAGEMENT

9.1 Several waste [illegible] GPL generates can be handled in a fairly routine manner. The [illegible] describing the method for waste disposal of chemicals including [illegible] and reagent solutions, and process waste, and samples is described [illegible] Standard Operating Procedures D.1 and D.2.

10.0 DEFINITIONS

10.1 For definitions of terms used in this document, refer to GPL Laboratory SOP G.14.

11.0 REFERENCES

- EPA Test Methods for Evaluating Solid Waste, SW846, Revision 0, December 1996.

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SOP No: M.5

Title: Volatile Organics - Method 8260B

1.0 SCOPE AND APPLICATION

1.1 This method is used to identify and quantify volatile compounds in aqueous, water, soil, and various types of waste samples using GC/MS methodology. The compounds listed below include the most commonly requested analytical parameters.

Target Compound List

[illegible]
Dichlorodifluoromethane
Chloromethane
Vinyl Chloride
Bromomethane
Chloroethane
Trichlorofluoromethane
Trichloroethene
1,1,2-Trichloro-1,2,2-Trifluoroethane
Acetone
Carbon Disulfide
Methyl Acetate
Methylene Chloride
Trans-1,2-Dichloroethene
Methyl tert-Butyl Ether
1,1-Dichloroethane
cis-1,2-Dichloroethene
2-Butanone
Chloroform
1,1,1-Trichloroethane
Cyclohexane
Carbon Tetrachloride
Benzene
1,2-Dichloroethane
Trichloroethene
Methylcyclohexane
1,2-Dichloropropane

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Bromodichloromethane
Cis-1,3-Dichloropropene
4-Methyl-2-Pentanone
Toluene
Trans-1,3-Dichloropropene
1,1,2-Trichloroethane
Tetrachloroethene
2-Hexanone
Dibromochloromethane
1,2-Dibromoethane
Chlorobenzene
Ethylbenzene
Xylenes (total)
Styrene
Bromoform
Isopropylbenzene
1,1,2,2-Tetrachloroethane
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,2-Dichlorobenzene
1,2-Dibromo-3-chloropropane
1,2,4-Trichlorobenzene

Acetonitrile
Acrylonitrile
Allyl chloride
2-Chloro-1,3-butadiene
Dibromomethane
trans-1,4-Dichloro-2-butene
p-Dioxane*
Ethyl methacrylate
Isobutyl alcohol
Methacrylonitrile
Methyl iodide
Methyl methacrylate
Pentachloroethane
Propionitrile*
1,1,1,2-Tetrachloroethane
Hexachloroethane
1,2,3-Trichloropropane
1,1-Dichloropropylene
1,4-Dioxane
** Acrolein
Bromochloromethane

*Poor purging efficiency /**poor performers resulting in high EDL.

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Additional Compounds

2, 2 - Dichloropropane
1, 3 - Dichloropropane
Bromobenzene
n - Propylbenzene
2 - Chlorotoluene
4 - Chlorotoluene
1, 3, 5 - Trimethylbenzene
tert - Butylbenzene
1, 2, 4 - Trimethylbenzene
sec - Butylbenzene
4 - Isopropyltoluene
n - Butylbenzene
Hexachlorobutadiene
Naphthalene
1, 2, 3 - Trichlorobenzene
Iodomethane

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TABLE 1

Comp No.	Compound Name	Quantitation Ion
1)	Dichlorodifluoromethane	85
2)	Chloromethane	50
3)	Vinyl Chloride	62
4)	Bromomethane	[illegible]
5)	Chloroethane	[illegible]
6)	Trichlorofluoromethane	[illegible]
7)	1,1-Dichloroethene	[illegible]
8)	1,1,2-Trichloro-1,2,2-Trifluoroethane	101
9)	Acetone	43
10)	Carbon Disulfide	76
11)	Methyl Acetate	[illegible]
12)	Methylene chloride	[illegible]
13)	trans-1,2-Dichloroethene	[illegible]
14)	Methyl tert-Butyl Ether	[illegible]
15)	1,1-Dichloroethane	[illegible]
16)	Cis-1,2-Dichloroethene	96
17)	2-Butanone	43
18)	Chloroform	83
19)	1,1,1-Trichloroethane	97
20)	Cyclohexane	56
21)	Carbon Tetrachloride	117
22)	Benzene	78
23)	1,2-Dichloroethane	62
24)	Trichloroethene	130
25)	Methylcyclohexane	83
26)	1,2-Dichloropropane	63
27)	Bromodichloromethane	83
28)	1,3-Dichloropropene	75
29)	4-Methyl-2-pentanone	43
30)	Toluene	91
31)	trans-1,3-Dichloropropene	75
32)	1,1,2-Trichloroethane	97
33)	Tetrachloroethene	164
34)	2-Hexanone	43
35)	Dibromochloromethane	129
36)	1,2-Dibromoethane	107
37)	Chlorobenzene	112
38)	Ethylbenzene	106
39)	Xylene (total)	106
40)	Styrene	104
41)	Bromoform	173
42)	Isopropylbenzene	105
43)	1,1,2,2-Tetrachloroethane	83

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44)	1,3-Dichlorobenzene	146
45)	1,4-Dichlorobenzene	146
46)	1,2-Dichlorobenzene	146
47)	1,2-Dibromo-3-Chloropropane	75
48)	1,2,4-Trichlorobenzene	180

*Poor performers.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into a gas chromat[illegible] and trap method.

2.2 An inert gas is bubbled through the solution at amb[illegible]t ter[illegible]eratur[illegible] temperatures for soil samples), and th[illegible] volatile c[illegible]onen[illegible] are e[illegible] transferred from the aqueous phase t[illegible]the vapo[illegible]se. [illegible] through a sorbent column where th[illegible]ts a[illegible] purging is comp[illegible]ted, the sorbent [illegible]nd b[illegible] gas to desorb the components onto a [illegible]raphi[illegible] chromatographic [illegible]umn is [illegible]ch are de[illegible]cted with a mass spec[illegible]

3.0 INTERFERENCES

3.1 Interf[illegible]ary considerably from source to sour[illegible]sample or extract being tested. The [illegible] be checked to ensure freedom from [illegible] All samples and QC samples must be [illegible]ces of contamination or carryover. If high con[illegible](s) are found in a sample, the next sample(s) on the seq[illegible]uld be checked for possible carryover. Concentrations [illegible] the highest levels of the calibration range are considered a [illegible] source of carryover. Usually those compounds that are quantified [illegible] the second and third internal standards (applicable to volatiles) may [illegible]use carryover. After the analysis of a sample containing high concentration of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the organic compounds present in the high level sample, freedom from contamination has been established. If the sample is suspected to have carryover, re-analysis should be performed. The ALS (Automatic Liquid Sampler) position that contained the sample with the high levels of contaminants needs to be marked and cleaned. The next sample loaded in that position needs to be monitored for any possibilities of carryover. The contaminated position and corrective action performed must be documented on the injection log. Contamination generated by non-target compounds also needs to be monitored. The level of carryover by non-target compounds should be compared to the internal standards. The significance of the non-target

compound carryover should be evaluated by the supervisor to determine the overall impact on the sample results.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatograph

Hewlett-Packard 5890 Gas Chromatographic Systems (GC) are employed for execution of this method. The GCs are complete with temperature programming capabilities, and all required accessories such as columns, [illegible], cutting [illegible] and syringes. Sample introduction is accomplished through [illegible] and trap systems.

4.2 Purge and Trap System

The Tekmar 2000/3000 purge and trap system [illegible] coupled with the [illegible] chromatographic system. The system is [illegible] with a [illegible] position autosampler, and a sample heating [illegible] for soil [illegible].

The purge and trap device [illegible] mode. The sample purger, the trap and the [illegible] purging chamber accepts glass vessels capable of holding [illegible] grams of soil samples. The glass tubes [illegible] prevent contamination from organic va[illegible]

The [illegible] cm long and has an inside diameter of [illegible] 10 [illegible] trap and marketed as VOCARB 3000 by vendors such as Supelco, [illegible] on.

A complete description of the inner workings of this purge and trap model is available in the Tekmar 2000/3000 manual.

4.3 Mass Spectrometer

The HP-5970 quadruple Mass Selective Detector is used as the detection device for Method 8260B. This system is capable of scanning from 35-260amu every one second or less, using 70 volts (nominal) electron energy in the EI mode. After proper tuning, the system produces a mass spectrum that meets all the criteria in Table 4 when 50ng of 4-Bromofluorobenzene (BFB) are injected into the gas chromatograph.

4.4 Data System

Each GC/MS system is attached to a dedicated 486 or pentium based computer equipped with Enviroquant software for automated acquisition and processing. The software generates total and extracted ion profiles of each compound and is capable of performing library searches on spectra using a full EPA/NIH Mass

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Spectral Data Library. Each system is attached to an internal laboratory computer network for additional data processing, storage and archiving.

4.5 Column

Megabore column, 60 meters in length, with a 0.53 mm internal diameter and 2.0 micron film thickness is used.

4.6 Microsyringes - 10ul, 25ul, 100ul, 250ul, 500ul, and 1000ul.

4.7 Luerlock syringe - 5 and 25ml gas tight.

5.0 REAGENTS AND STANDARDS

5.1 Organic free reagent water.

5.2 Stock solutions.

5.3 Methanol, High purity grade, P.& [illegible] and Ti[illegible]aly[illegible].

6.0 SAMPLE COLLECTION [illegible]

6.1 Water sample[illegible] having a total volume of at least 40ml[illegible] open top screw-cap. Soil samples may [illegible] glass containers or closed end tubes (e.g., brass sleeves) in sufficient quantity to perform the analysis. Headspace should be avoided. The [illegible] requirements for sample collection are outlined by the Region.

[illegible] collection of water samples, the containers must be filled in such a manner that no air bubbles pass through the sample as the container is being filled. Seal the [illegible] so that no air bubbles are entrapped in it.

[illegible] samples are preserved to a pH of 2 at the time of collection.

[illegible] All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until analysis.

6.5 All water and soil samples must be analyzed within 14 days of collection.

7.0 METHOD DETECTION LIMIT

7.1 Method detection limits for this method are listed in the GPL Laboratory Method Detection Limit and Reporting Limit official book.

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8.0 METHOD PERFORMANCE

8.1 The MDL concentrations listed in the GPL MDL book are generally obtained using organic-free reagent water. Results were also obtained by extracting seven spiked replicates the same way as the samples and analyzing them. MDL is defined as the minimum concentration of a substance that can be measured and a reported with 99% confidence that the value is above zero. Precision and accuracy studies are performed once a year at a minimum. Single operator precision, overall precision and method accuracy were found to be directly related to the concentration of the parameter.

9.0 CALIBRATION AND STANDARDIZATION

9.1 Calibration

Five concentration levels are analyzed for each analyte and surrogate standards. A minimum five point curve is the [illegible] point [illegible]. Calibration levels are analyzed at [illegible] and/or [illegible] for analytes and surrogate standards [illegible] which is analyzed at 40, 100, 200, 300 and 400 [illegible].

9.2 Instrumentation P[illegible]

The following [illegible] operating [illegible] for method 8260B.

Electron energy:	[illegible] volts (nominal)
Mass range:	35-260amu
Scan time:	Not to exceed 1 second/scan
Initial column temperature:	10° C
Initial column holding time:	4 min
Column temperature program:	8° C/minutes
Final column temperature:	190° C
Final column holding time:	1 min
Injector temperature:	220° C
Source temperature:	According to manufacturer's specifications
Transfer line temperature:	280° C (Preset to manufacturer)
Carrier gas:	Helium at about 8ml/min

9.3 Tuning

9.3.1 At the beginning of each day, each GC/MS system is injected with 50ng of BFB and tuned to meet the criteria listed in Table 4. The analysis must not commence unless the criteria are met. This requirement must be met for each 12 hour interval.

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9.3.2 One of the following approaches is used to evaluate the BFB tune.

- One scan at the apex without background subtraction.
- Three scans (the apex peak scan and the scan immediately preceding and following the apex) are acquired and averaged.
- Use the mean of the apex and the preceding of the following scans
- Use the average across the entire peak.

9.4 Calibration Requirements

Once tuning requirements are met, the initial or continuing calibration [illegible] must be established. The general [illegible] factors [illegible] establishing the calibration requirements [illegible] 8260[illegible]. The [illegible] for determining the response factors are [illegible]

9.4.1 Tabulate the area [illegible] ions [illegible] Table 1) against the concentration [illegible] and each internal standard. Calculate [illegible] RF [illegible] compound relative to one of the internal [illegible] selected for the calculation of the [illegible] compound should be [illegible] internal standard with the retention [illegible] to the compound being measured. The RF is calculated as follows:

$$RF = \frac{(A_x)(C_{is})}{(A_{is})(C_x)}$$

where:

A_x	Area of the characteristic ion for the compound being measured
A_{is}	Area of the characteristic ion for the specific internal standard.
C_{is}	Concentration of the specific internal standard.
C_x	Concentration of the compound being measured.

The average RF must be calculated for each compound. A system performance check should be completed before the calibration curve is used. Five compounds, the System Performance Check Compounds, or SPCCs, are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene (see Table 3). The minimum relative response factors for these compounds should be 0.1, 0.1, 0.1, 0.3 and 0.3. These compounds typically have RFs respectively, of 0.4-

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0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Initial calibration is analyzed at a minimum of 5 levels. These levels are 5, 20, 50, 100, 150 and/or 200ug/l. The following compounds have higher initial calibration levels.

Acrolein	100	250	500	750	1000
Acrylonitrile	100	250	500	[illegible]	1000
2 - Chloroethyl Vinyl Ether	80	200	400	[illegible]	[illegible]

Using the RFs from the initial calibration, calculate the percent relative standard deviation (% RSD) for all compounds.

% RSD = SD X / X

where:

RSD = relative standard deviation
X = mean RF for a compound
N = number of calibration points
SD = standard deviation of the RFs for a compound
X_i = response factor for each point

$$SD = \sqrt{\frac{\sum_{i=1}^{N} (X_i - X)}{N-1}}$$

[illegible] After analyzing the initial calibration standard, average response factor (RF) should be calculated for each compound. The percent relative standard deviation %RSD should be equal or less than 15% for each compound However, Calibration Check Compounds (CCC's) must have a %RSD less than or equal to 30%. It is likely that some analytes may exceed the 20% acceptance limit for the %RSD. In those instances the following steps should be considered:

- If the %RSD is greater than 20%, the analyst should review the results (area counts, response factors, standard concentrations) for those analytes to ensure that the problem is not associated with a single standard. If so, that standard should be reanalyzed and RSD recalculated. Replacing of standard may be necessary in some cases.

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- It may also be necessary to narrow the calibration ranges to achieve a better linearity. High standard may saturate the column or/and the detector and need to be dropped from the calibration curve accordingly. Similarly poor purging compounds that exhibited erratic chromatographic behavior in the lowest calibration point could also be reviewed and dropped if necessary. The changes to the upper end of the calibration will affect the need to dilute samples above that range, while the change to the lower calibration will affect the sensitivity and elevate the reporting limit of the method. When considering dropping one or two points to narrow the calibration range, a minimum of five points is required for curve to be acceptable.

9.4.2.1 After visual inspection of the calibration points for each analyte and for those analytes that did not meet the %RSD criteria at the discretion of the analyst should consider the [illegible] equation that does not [illegible] through origin or quadratic (second order) model. Linearity is [illegible] acceptable if the correlation coefficient (r) is equal to or greater than 0.9[illegible]

9.4.2.2 If linear [illegible] curve does not fit the response being observed [illegible] considered as an option. [illegible] correlation coefficient (r^2) [illegible] greater than [illegible]

9.4.2.3 [illegible] implementation of the above alternatives, some of the compounds [illegible] listed in the compound list may exceed the [illegible] acceptance criteria. The initial calibration may still be acceptable if the mean of the RSD values for all analytes in the calibration is less than or equal to %15. The mean RSD is calculated by summing up the RSD value for each analytes and dividing by the total number of analytes in the calibration standard regardless whether or not they are compound of interest. The approach should be used only when limited number of poor performing compounds exceeded the 20% RPD but inside the 40% established limit. When this approach is used the data user should be aware that the use of this approach might lead to greater uncertainty for those analytes for which RSD is greater than 20% The laboratory should communicate the following information within the case narrative to the client:

- summary of all target analytes exceeding method acceptance criteria
- the individual RSD results for those compounds
- and the mean RSD calculated

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9.4.2.4 Prior to use for sample analysis, the acceptability of initial calibration curve must be verified through analysis of calibration verification (ICV) solution obtained from second source. Calibration verification analysis should meet the same acceptance criteria used for continuing (daily) calibration.

9.4.3 Continuing (Daily) Calibration

The initial calibration curve for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a 50ppb calibration standard and verifying all compound of interest meet the acceptance criteria for daily calibration. Daily calibration standard analysis must meet the relative response factor criteria for SPCC and non SPCC % difference criteria of calibration check compounds (CCC) and non CCC. If SPCC and non SPCC criteria listed in Table 3 are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Potential problem include standard mixture degradation, system inlet contamination, contamination of front end of the analytical column, and active sites in the chromatographic system. After the criteria for relative response factor of RRF is met, calculate the % difference to confirm the validity of the initial calibration.

Calculate the % difference using the following equation:

$$\text{Difference} = \frac{RRF_c - \overline{RRF_i}}{RRF_i} \times 100$$

Where:

RRF_c Relative response factor from continuing calibration standard

$\overline{RRF_i}$ Mean relative response factor from the most recent initial calibration meeting technical acceptance criteria

If the 20 percent difference for each CCC and non-CCC (except 8 poor purging or performing compounds that could have %D less than or equal to 40%) did not meet, corrective action should be taken. After corrective action, if the source of the problem can not be determined, a new five point calibration MUST be generated. This criteria must be met before sample analysis begins. The internal standard response and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. Tables 2 and 3 list SPCC and CCC compounds.

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9.5 Retention Time and Area Change

9.5.1 If the retention time of any internal standard of a sample or QC sample change by more than 30 seconds from the daily calibration verification standard or if the daily calibration verification standard change by more than 30 seconds from mid level standard of the latest initial calibration corrections must be made. Affected samples must be reanalyzed after problem is corrected.

9.5.2 If internal standard area in the samples changes by [illegible] factor [illegible] (-[illegible] to +100%) from the calibration standard verification, c[illegible] made. After corrections reanalysis of samp[illegible] was malfunctioning is required. Area of the [illegible]ily c[illegible] verification must not change by a factor of t[illegible] (-50[illegible] to +1[illegible] in the midpoint standard of the most rece[illegible]tial c[illegible]

10.0 DATA ANALYSIS AND CALCULATION

10.1 Qualitative Analysis

10.1.1 The com[illegible] identifi[illegible] by an analyst by comparis[illegible] the mass spectrum of a stand[illegible] criteria must be satisfied to ve[illegible]

10.1.[illegible] R[illegible] of the sample and standard must agree [illegible]

[illegible] pondence of the sample component and standard [illegible]ponent mass spectra.

[illegible] The requirement for qualitative verification by comparison of mass spectra are as follows:

All ions present in the standard mass spectra at a relative intensity greater than 10% <u>must</u> be present in the sample spectrum. All ions specified must agree within ±20% between the standard and sample spectra. Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for.

10.2 Quantitative Analysis

When a compound is identified, quantification is based on the integrated abundance of the primary characteristics ion and the response and amount of the corresponding internal standard.

$$\text{Concentration (ug/L)} \quad \frac{(Ax)(Iis)(D)}{(Ais)(Avg\ RF)(Vo)}$$

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$$\text{Concentration (ug/kg)} \quad \frac{(Ax)(Is)(D)}{(Ais)\ (Avg\ RF)\ (W)\ (S)}$$

where:

Ax	Area of primary ion
Is	Amount of internal standard, ug/L
Ais	Area of ion for internal standard
Avg RF	Mean relative response factor for compound [illegible]
Vo	Volume of sample purged, L
D	Dilution factor
W	Weight in Kg
S	% Solid

10.3 For non-TCL components, a library search may be executed [illegible] target organic compounds shall be [illegible] with [illegible] Guidelines for making tentative identifications.

10.3.1 Ions greater than [illegible]% of the most abundant ion should be present in the sample spectrum.

10.3.2 [illegible] should agree within ±20%.

10.3.3 [illegible] present in the reference spectrum should be present in the sample spectrum.

10.3.4 [illegible] in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

11.0 PROCEDURE

11.1 Sample Preparation

11.1.1 For sample preparation and introduction of close system purge and trap and extraction of soil and water volatile compounds to the mass spectrometer, refer to GPL SOP M.7.

11.2 Water Samples

11.2.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

11.2.2 BFB tuning criteria and daily GC/MS calibration criteria must be met before analyzing samples.

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11.2.3 Adjust the purge gas (Helium) flow rate to approximately 40ml/min on the purge and trap device.

11.2.4 Remove the plunger from a 5ml syringe. Open the sample and carefully pour the sample into the syringe barrel to just short of overflowing. Compress the sample. Vent any residual air while adjusting the sample volume to 5.0ml

11.2.5 Add 5.0ul of surrogate spiking solution and 5ul of internal standard solution (50ppm each) through the valve bore of the syringe and load samples into the sample tube. Immediately after loading the sample, verify the pH of the samples using narrow range pH paper. Samples should not be opened to verify pH prior to loading into the purge unit.

11.2.6 Lab Control Spikes (LCS) are analyzed per batch or every [illegible] and at the same frequency as the method blank. LCS is spiked with all target compound of interest. The LCS recoveries must be within the in-house established control limit. Statistically calculated limits are based on data points. Data points used in the initial calculation should not be arbitrarily included or excluded. If recoveries of the LCS compounds fall outside the established control limits, corrective action must be taken. After corrective action, if LCS recoveries fall outside QC acceptance limits, all the associated samples must be reanalyzed. No compound can exceed 50%-150%

11.2.7 For the matrix spike analysis, add 5ul of the matrix spike solution [illegible] to be purged. This will yield a final concentration [illegible] (5ug/liter for [illegible]) in the final sample. Matrix spike QC sample [illegible] target analytes of interest. (See Section 9.5 for criteria).

11.2.8 Specimen samples are analyzed with appropriate dilution when the concentration level of any analyte exceeds the calibration range. Dilutions are made in the 5ml gas tight luer lock syringe by adding reagent water. Calculate the volume of reagent water needed for the dilution and add into a 5ml syringe. Dilution of samples should result in analysis with the highest concentration target analyte in the upper half of the calibration range. Using a suitable syringe, add the exact volume of sample into the reagent water in the 5ml syringe. Add 5ul of Internal Standard & Surrogate and analyze as discussed above. If the dilute sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution.

11.2.9 The spiked sample is injected into a purging tube attached to the Purge & Trap device. Purge the sample for 11 minutes and desorb the contents of the trap at 200° for 2 minutes into the GC/MS.

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11.2.10 Low Concentration Method: This method is applicable to water samples containing low levels of contaminants. The detection limits are generally improved by analyzing larger sample volume (25ml). The detection limits of compounds with poor purging efficiency (such as ketones) do not significantly improve when low concentration method is utilized. The low concentration analytical procedure is virtually the same as low level water analysis except for concentration of the calibration, surrogate and internal standards. The following concentration levels and ranges are analyzed:

Calibration	-	.5, 10, [illegible], [illegible], [illegible]
Surrogates	-	.5, 10, [illegible], 40, [illegible]
Internal Standards	-	10 [illegible]g/L
Continuing Calibration	-	[illegible]g/L

Acceptance criteria for the [illegible] continuing [illegible] are the same as the normal [illegible] Criteria for [illegible] and difference in the initial [illegible] calibration are described in section 8.4. [illegible] for the [illegible] or purging [illegible] [illegible]

11.2.11 [illegible] analysis, the purge and trap cells are [illegible] The purge and trap cells are cleaned [illegible] and mild soap, and rinsed with deionized [illegible] and trap cells are then baked in an oven at [illegible] for at least four hours. Upon completion of baking, the [illegible] and trap cells are placed in a container covered with [illegible] foil.

11.3 [illegible] and Waste Samples

11.3.1 Low Concentration method: Applicable for samples containing individual compounds of <1mg/kg. All granular/porous waste/sediment/soil samples can be analyzed using this method.

Weigh 5g of the sample into a glass sparge tube and record the weight to the nearest 0.1g. Add reagent water to a 5ml luerlock type syringe and adjust the volume to 5ml. Add 5ul of internal standard and 5ul of surrogate standard to the water. Connect the sparge tube with the sample to the purge & trap device and add the spiked water to the sample. Heat the sample to 40°C ±1°C and purge the sample for 11 minutes. Desorb the trap at 200°c for 2 minutes into the GCMS.

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If the concentration level of any analyte exceeds the calibration range and is below 1mg/kg, the sample should be analyzed by weighing 1g of the sample. If the concentration level of any analyte is higher than 1mg/kg, then the high concentration method should be used.

11.3.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

11.3.3 BFB tuning criteria and daily GC/MS calibration criteria must be met before analyzing samples.

11.3.4 Adjust the purge gas (Helium) flow rate to approximately 40 ml/min in the purge and trap device.

11.3.5 Weigh 5.0 grams of the soil sample into a closed purge device using a top loading balance. Note and record the actual weight to the nearest 0.1g. Quickly connect the device to the purge and trap system.

11.3.6 Prepare a reagent water containing 5 ml surrogate, 5.0 ml of internal standard solution (50ppm each). Inject this solution through the valve pore of the syringe into the vial sample tube.

11.3.7 Lab Control Spike (LCS) is analyzed per batch or every 20 samples and is prepared from the method blank. LCS is spiked with all target compounds of interest. LCS compound must be within the in-house established control limit. Statistical control limit are based on 20 data points. Data points used in the data set must not be selectively included or excluded. If recovery of more than two LCS compounds fall outside the established limit, corrective action must be taken. After corrective action, LCS analyte recovery is still outside QC acceptance limits, all associated samples batch must be reanalyzed. No compound can exceed grossly the acceptance limit of 50%-150%.

11.3.8 For the matrix spike analysis, add 5ul of the matrix spike solution (50ppm) to the sample to be purged. This will yield a final concentration of 50ug/L (ug/kg for soils) in the final sample. Matrix spike QC sample must contain all target analytes of interest.

11.3.9 High Concentration Method: The method is based on extracting the soil/sediment with methanol. Weigh 4gm of the sample into a 20ml vial using a top loading balance. Record the weight to the nearest 0.1g. Using a pipet, add 9.0ml methanol; then add 1.0ml of the surrogate spiking solution into the vial. Close the cap and shake for 2 minutes. Pipet approximately 1ml of the extract to a GC vial for storage, using a disposable pipet. Transfer approximately 1ml of the method blank to a separate GC vial for each set of samples. The standards, LCS and blanks should contain 100µl of a solvent to simulate the sample condition. 100ul of the extract is added to reagent water collected in a 5ml luerlock

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syringe. 5ul each of Internal Standard is added to the syringe. Proceed with the analysis as outlined in the water sample analysis. If further dilution is needed, a smaller extract volume is used and the same procedure is repeated

A separate method blank containing 100ul methanol should be analyzed prior to a high concentration sample.

11.3.10 For matrix spike in the high concentration sediment/soil samples, 8.0ml of methanol, 1.0ml of surrogate spike solution, and 1.0ml of spike solution is added to a 4g sample. Cap and shake for 2 minutes. Add a 100µl aliquot of this extract to 5ml of reagent water for purging.

11.3.11 Samples extracted through Toxicity Characteristic Leaching Procedure by zero headspace extractor are analyzed by the method. Only those compounds designated by the GC/MS method are accounted for. The pH of the extract is adjusted to 10 in order to minimize the acetic acid on the chromatograph and purge and trap system.

12.0 QUALITY CONTROL

12.1 Prior to initiating the analysis, it must be verified that the GC/MS meets BFB abundance criteria. Take a daily (12) hour period for the method.

12.2 If the (12) hour has elapsed since the initial tune, the GC/MS must be retuned to meet the criteria.

12.3 Internal standard responses and retention times in the calibration checks, blanks and samples must be evaluated. Retention time variation of any internal standard in the calibration standard must be less than 30 seconds from that in the mid point standard in the calibration standard. All other samples and QC samples must be compared to the daily CCV and should not vary by more than or equal to 30 seconds. If this criteria exceeds samples that did not meet the criteria should be re-injected.

12.4 Surrogate recoveries must be evaluated by determining whether the concentrations fall inside the internal QC limits. If surrogate recoveries falls outside the established QC limits, then analyze the sample that fail the criteria.

12.5 A matrix spike and spike duplicate must be performed every tune or 20 samples, whichever comes first, at the concentration equal to mid-level calibration (50ug/l). If matrix spike QC recoveries does not meet established acceptance criteria, the analyst and the manager must assess the batch to determine whether the spike results are attributable to matrix affect, or the result of other problems in analytical process. If all batch QC elements which are not affected by matrix are in control (e.g., method blank, LCS) the poor recovery may be attributed to

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matrix affect. If the native concentration is low, and the MS/MSD recoveries confirm matrix interferences, dilute the MS/MSD and reanalyze. TCLP samples are spiked with TCLP target compounds at 50ug/l concentration.

12.6 QC limits for MS/MSD, LCS and surrogates are established and published yearly for internal use

12.7 A method blank must be performed for each 12 hour time period.

12.7.1 A method blank for volatile analysis must contai[illegible] than pr[illegible] ½ of the reporting limits. Any method blank ass[illegible] samples must comply with the following criteria.

- If the concentration of target analyte [illegible] the [illegible]thod [illegible] is greater than MDL but less than N[illegible]eport[illegible] limit [illegible] purging apparatus with two [illegible]ganic [illegible] and reanalyze the [illegible] [illegible] corr[illegible] if level contamination [illegible] [illegible]socia[illegible] may be reported with qu[illegible]

- If t[illegible] [illegible]te in the method blank is gr[illegible] [illegible]y be necessary to wash the [illegible]se it with organic free [illegible] purging device in an oven at [illegible] analyzed before the contamination [illegible]

12.8 [illegible] (LCS) a[illegible]nalyzed per batch or every 20 samples and at the [illegible] method blank. LCS is spiked with all target compound of inte[illegible] and must be within the in-house established control limit. Sta[illegible] limit are based on 20 data points. Data points used in the data [illegible] be selectively included or excluded. If recovery of more than two [illegible]pounds fall outside the established limit, corrective action must be [illegible] After corrective action, if LCS analyte recovery is still outside QC [illegible]cceptance limits, all the associated samples batch must be reanalyzed. No compound can exceed grossly the acceptance limit of 50%-150%.

12.9 For samples received from the state of California, travel blanks will be prepared and analyzed for each batch of samples.

13.0 SAFETY

13.1 Safety glasses, laboratory coats, and latex gloves must be worn.

13.2 Due to the toxicity or carcinogenicity of each reagent, each chemical compound should be treated as a potential health hazard.

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13.3 Material Safety Data Sheets (MSDS) can be found on the procurement bookshelves located in the administrative area.

13.4 Standard preparation should be handled under a hood.

14.0 POLLUTION PREVENTION

14.1 GPL Laboratory operates in a safe manner to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. For more detail on pollution prevention, refer to GPL SOP D[illegible]

15.0 WASTE MANAGEMENT

15.1 Several wastes that GPL generates can be handled in a fa[illegible] routi[illegible] The process of describing the method for waste disposal of chemi[illegible] standards and reagent solutions, [illegible] and [illegible] in Standard Operating Procedures [illegible]2.

16.0 DEFINITIONS

16.1 For definitions of terms [illegible] GPL Laboratory SOP G.14.

17.0 REFERENCES

- Test[illegible] Physical/Chemical Methods, SW846, [illegible] 1996.

- [illegible] Laboratory Quality Assurance Guide, February 199[illegible]

- [illegible] Document, Version 1.0, November 1998.

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TABLE 2

CALIBRATION CHECK COMPOUNDS

1 - 1,1-Dichloroethene

2 - Chloroform

3 - 1,2-Dichloropropane

4 - Toluene

5 - Ethylbenzene

6 - Vinyl chloride

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TABLE 3

SYSTEM PERFORMANCE CHECK COMPOUNDS

1 - Chloromethane

2 - 1,1-Dichloroethane

3 - Bromoform

4 - 1,1,2,2-Tetrachloroethane

5 - Chlorobenzene

All other compounds must meet a minimum RF of 0.050

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TABLE 4

BFB KEY ION ABUNDANCE CRITERIA

Mass	Ions Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

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SOP NO: S.6

Title: Measurement of Polynuclear Aromatic Hydrocarbons in Water and Soil by High Performance Liquid Chromatography (HPLC).

1.0 SCOPE AND APPLICATION

1.1 This method is used to identify and quantitate [illegible] and sub-[illegible] polynuclear aromatic hydrocarbons (PAH's) in water and soil by HPLC fluorescence detection coupled with UV detection. The method is based on EPA method 8310.

[illegible] Compound List

Naphthalene
Acenaphthene
Acenaphthylene
Fluorene
Phenanthrene
Anthracene
Fluoranthene
Benzo(a)anthracene
Pyrene
Chrysene
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(a)pyrene
Dibenz(a,h)anthracene
Benzo(g,h,i)perylene
Indeno(1,2,3,c,d)pyrene

2.0 SUMMARY OF METHOD

2.1 The PAH's are extracted from water and soil with organic solvent, concentrated and injected into an HPLC equipped with a fluorescence detector and a UV detector in series. The sixteen PAH's are separated on a specialty LC column using an acetonitrile: water mobile phase operated at a gradient over 40 minutes. Fourteen PAH's are identified and quantitated on the fluorescence detector and two PAH's are identified and quantitated on the UV detector at 254nm.

3.0 INTERFERENCES

3.1 Solvents and reagents may contain artifacts which may affect chromatography and/or analyte seperation. All solvents used must be UV grade and filtered using a 0.45um filter to degas and remove particulates. Water is de-ionized and filtered. The method blanks must be demonstrated to be free of contaminants.

3.2 Interferences present in a particular matrix are handled by the following.

3.2.1 A matrix interference on the fluorescent detector may not be present on the UV detector. Depending on the affected analyte and analyte sensitivity, quantitation may be performed on the UV detector.

3.2.2 Particular soil sample extracts may require pre-analysis [illegible] or dilution to minimize or eliminate the effect of matrix [illegible]

4.0 APPARATUS AND MATERIALS

4.1 Apparatus

- Amber [illegible] Glass vials, 4ml with [illegible] caps
- 1 [illegible]
- Syringes, 1ml, 50ul, 100ul and 25ul.
- PTFE membrane filters, 0.45um

4.2 HPLC Equipment

- The analytical instrumentation and conditions are listed in Table 1.

4.3 Data System

- Enviroquant, Hewlett Packard

5.0 REAGENTS

- Deionized, organic free water.
- Acetonitrile, Burdick Jackson UV Grade
- Certified Individual PAH standard stock solutions (1000ug/ml), Protocol.
- Surrogate Standard, p-Terphenyl, Aldrich Chem. Co.

6.0 METHOD DETECTION LIMIT

6.1 Method detection limits for this method are listed in the GPL Laboratory Method Detection Limit and Reporting Limit official book.

7.0 METHOD PERFORMANCE

7.1 The MDL concentrations listed in the GPL MDL book are generally obtained using organic-free reagent water. Results were also obtained by extracting seven spiked replicates the same way as the samples and analyzing them. MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. Precision and accuracy studies are performed once a year at a minimum. Intra-method precision, overall precision and method accuracy were found to be directly related to the concentration of the parameter.

8.0 SAMPLE COLLECTION, HANDLING AND HOLDING TIMES

8.1 Water samples may be collected in 1L or (two) amber glass containers. Soil samples may be collected in glass containers or closed sample bags.

8.2 All samples must be held at refrigerated at 4°C (±2°C) from the time of collection until extraction.

8.3 Extraction holding times for water is seven days from the date sampled ad fourteen days from the date sampled for soil. Analysis holding time is 40 days from the date of extraction for both soil and water samples.

9.0 PROCEDURE

9.1 Water and Soil Extraction

9.1.1 Refer to SOP for the procedure for extracting water using EPA method 3510 (separatory funnel) and SOP for EPA method 3520 (continuous extraction).

9.1.2 Refer to SOP for the extraction procedure of soil using EPA method 3550 (sonication).

9.1.3 Prior to HPLC analysis the extraction solvent must be exchanged into acetonitrile (1ml). The procedure is as follows. After cooling, the extraction solvent (~ 10ml) is concentrated to 0.5ml in a concentrator tube under a gentle stream of N2 gas at 35°C. The solvent is exchanged by adding 2.0ml of acetonitrile and concentrating the solvent mixture to 1.0ml. The 0.5ml methylene chloride will evaporate first leaving the final solvent as acetonitrile. The final extract is stored at 4°C.

9.2 Calibration Standards: The fluorescence and UV detectors are calibrated using external standards. Intermediate standards (10ug/ml) are prepared by adding 100ul of each PAH from the stock (1000ug/ml) to 10ml of acetonitrile. A working standard is prepared by adding various amounts of each individual analyte stock or intermediate solution (1000 or 10ug/ml) into acetonitrile to achieve a combined mixture which produces relatively the same responses for all analytes. The amount of each analyte and the respective concentration is provided in Table 2.

9.3 Initial calibration: Five calibration standards are used for the initial calibration of each detector. The five levels are designated as CALSTD1, CALSTD2, CALSTD3, CALSTD4 and CALSTD5. The initial calibration standards are prepared by diluting the working standard (WS) into acetonitrile as follows.

CALSTD1	100ul of WS into 900ul [illegible]
CALSTD2	250ul of WS into 7[illegible]ul [illegible]
CALSTD3	500ul of WS into [illegible]
CALSTD4	750ul of WS into [illegible]
CALSTD5	1000ul of WS [illegible] (no [illegible])

The concentration of each analyte in each initial calibration solution is provided in Table 3.

The ratio of analyte to peak area, calibration factor (CF), is determined for all analytes and the percent relative standard deviation (% RSD) of the calibration factors should be less than 20% over the working range. Linearity through the origin can be assumed and the average response factor can be used for quantitation.

$$\%RSD = \frac{SD}{X} \times 100$$

Where:

SD = Standard deviation of CFs
X = Mean of 5 initial CFs

An Initial Calibration Verification standard must be analyzed immediately after the calibration curve. This standard must be prepared from a source different than that used to prepare the calibration curve standards. The concentration must be near the mid-range of each compound's calibrated range. The %Deviation for all compounds must be less than 25%.

9.4 Continuing Calibration: A calibration standard at mid-level (CALSTD3) is analyzed at the beginning of an analytical run, every 10 samples or twelve hours, and at the termination of an analytical sequence. The percent difference (% D) of the continuing calibration should be less than 25% for each analyte. If one or two compounds have % D outside the limits, the standard is still within control

limits if the average % D for the standard is less than 25%. Repeated failures of the same compound, however, would indicate a deviation from the calibration curve, and a new curve should be analyzed.

$$\% D = \frac{CF_i - CF_c}{CF_i} \times 100$$

where:

CF_i = average calibration factor from initial calibration
CF_c = calibration factor from current calibration check standard

The average calibration factor from the initial curve is used for sample quantitation if the continuing calibration criteria are met.

9.5 Retention Time Establishment

A retention time window for each analyte is established periodically by calculating the standard deviation of the retention times of the low level standards analyzed over no fewer than [illegible] days. The window is computed as plus and minus 3 times the standard deviation. The minimum retention time window for this method should be ± 0.2 minutes or the peak width of the analytes chromatographed by HPLC.

9.6 Sample Analysis

Samples are analyzed using the instrumentation and conditions outlined in Table 2. The fluorescence detector is installed as the first detector followed by the UV detector because the fluorescence flow cell operates more effectively (less susceptible to air bubbles) when there is added back pressure. After successful calibration the sample extracts may be analyzed. A blank containing acetonitrile should be analyzed immediately following analysis of an extract containing high background and/or target compounds. Sample extracts must be diluted so that the response of the highest analyte is within the calibration range. The UV detector can be used for confirming the identity and quantitation of ten analytes detected by the fluorescence detector.
Soil samples concentrated to 1ml for low level analysis typically contain both dissolved and undissolved co-extractives, especially high organic content soils. It is recommended that extracts be filtered using a 0.45um membrane filter to remove undissolved particulates prior to analysis. In addition, dissolved background substances in soil extracts often elevate and distort the fluorescence detector baseline, thus requiring dilution of the soil extracts prior to analysis.

Example retention times for each analyte and detector are listed below. The analytes not detected at the calibration concentrations are designated with an ND.

PAH Analyte	Retention Time Fluorescence	Retention Time UV 254
Naphthalene	12.96	ND
Acenaphthene	17.50	ND
Acenaphthylene	ND	13.11
Fluorene	18.18	18.30
Phenanthrene	18.94	19.05
Anthracene	19.47	19.58
Fluoranthene	19.84	[illegible]
Pyrene	20.14	[illegible]
p-Terphenyl Surr. Std.	20.46	[illegible]
Benzo(a)anthracene	21.04	ND
Chrysene	21.80	ND
Benzo(b)fluoranthene	[illegible]	26.56
Benzo(k)fluoranthene	[illegible]	[illegible]
Benzo(a)pyrene	[illegible]	[illegible]
Dibenz(a,h)anthracene	[illegible]	[illegible]
Benzo(g,h,i)perylene	[illegible]	[illegible]
Indeno(1,2,3,c,d)pyrene	ND	[illegible]

9.7 Quantitation

The reporting limit (RL) for each PAH analyte is based on the concentration of the lowest calibration standard. The concentration of target analytes in water is determined by the following equation.

$$\text{Conc ug/L} = \frac{(\text{ug/ml Target PAH})(Fv)(DF)}{Sv}$$

Where:

ug/ml Target PAH	=	Concentration determined from initial calibration
Fv	=	Final Extract Volume, ml
Sv	=	Sample Volume, liters
DF	=	Dilution Factor

The concentration of target analytes in soil is determined by the following equation.

$$\text{Conc ug/Kg} = \frac{(\text{ug/ml Target PAH})(Fv)(DF)}{Sa\ (\%\ \text{Solids}/100)}$$

Where:

ug/ml Target PAH	=	Concentration determined from initial calibration
Fv	=	Final Extract Volume, ml
Sa	=	Sample Amount, Kg
DF	=	Dilution Factor

10.0 QUALITY CONTROL

10.1 The initial calibration curve must have a %RSD for the calibration factors of less than or equal to 25%. Continuing calibration standards and continuing verification standards must have percent differences less than 25%.

10.2 Water and soil samples must be extracted within [illegible] and [illegible] days, respectively, from the sampling date. Sample extracts must be analyzed within 40 days of the extraction date.

10.3 Water and soil method detection limit data, precision and recovery data are to be determined annually.

10.4 Control charts are to be established and maintained for surrogate recoveries in water and soil, laboratory control standards, matrix spike/matrix spike duplicate recoveries.

10.5 Laboratory control standards are extracted and analyzed with each sample batch per matrix. PAH analytes are added to an inert matrix at a level to correspond with the mid-level calibration standard.

10.6 Multiple matrix spike duplicate analyses are performed on a select sample per batch or for every 20 samples, whichever occurs first. PAH analytes are spiked at a level to correspond with the mid-level calibration standard.

10.7 Method blanks are extracted every batch of 20 samples or less. Blanks must be free of target analytes (levels below the reporting limits).

11.0 SAFETY

11.1 Always wear safety glasses or a shield for eye protection, gloves and lab coat.

11.2 Observe proper mixing when working with reagents and chemicals. Preparation of samples and standards should be handled under the hood.

11.3 A reference file of material data handling sheet is available to all personnel involving in these analyses.

12.0 POLLUTION PREVENTION

12.1 GPL Laboratory operates in a safe manner to protect the air, water, and land by minimizing and controlling all releases from fume hoods and a bench operations. For more detail on pollution prevention, refer to GPL SOP D.5.

13.0 WASTE MANAGEMENT

13.1 Several wastes that GPL generates can be handled in a fairly routine manner. The process of describing the method for waste disposal of chemicals including standards and reagent solutions, and process waste, and samples is described in Standard Operating Procedures D.1 and D.2.

14.0 DEFINITIONS

14.1 For definitions of terms used in this document, refer to GPL Laboratory SOP G.14.

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TABLE 1
EPA METHOD 8310 INSTRUMENTATION AND CONDITIONS

INSTRUMENTATION

Waters Pump, Model 510 for Mobile Phase (A)
Waters Pump, Model 510 for Mobile Phase (B)
Waters Automated Gradient Controller
Shimadzu Fluorescence Detector, Model RF-535 (Detector 1)
- Excitation wavelength = 208nm
- Emission wavelength = 380nm
- Sensitivity = High

Waters UV Variable Wavelength Detector, Model 484 (Detector [illegible])
- UV wavelength = 254nm
- Sensitivity = 0.01 AUFS

Waters WISP Autosampler, Model 712
Supelco Specialty HPLC Column: PHENOMENEX [illegible] SEPP[illegible] 4.6mm ID (5um)
Column Heater, Keystone Scientific
Waters Guard-Pak Precolumn C[illegible]

CONDITIONS

Mobile Phase: 40% [illegible] CH3N[illegible]
A = Acetonitrile (ACN)
B = Water

Column Temp: 25°C
Flow: 1.5 mL/min
Run Time: 45 min
Injection Vol: 25[illegible]

Mobile Phase Gradient Program

Time	Flow	%A	%B	%C	Curve
Initial	0.1	40	60	0	*
0.01	1.5	40	60	0	6
5.00	1.5	40	60	0	6
30.00	1.5	100	0	0	6
30.01	1.5	100	0	0	1
50.00	1.5	100	0	0	1
50.01	1.5	40	60	0	1
52.00	1.5	40	60	0	1
60.00	0.1	40	60	0	1

Table 2
PAH Calibration Standard Preparation – EPA Method 8310

WORKING STOCK (WS)

Fluorescence	Initial Conc., ug/ml	Vendor	Initial Amount,ul	Final Volume, ml	Final Conc. ug/ml	Solvent
Naphthalene	1000	Protocol	500	25	[illegible]	ACN
Acenaphthene	1000	Protocol	50	25	[illegible]	ACN
Fluorene	1000	Protocol	100	25	[illegible]	ACN
Phenanthrene	10	Protocol	1250	[illegible]	[illegible]	ACN
Anthracene	10	Protocol	2500	[illegible]	[illegible]	ACN
Fluoranthene	1000	Protocol	250	[illegible]	10	ACN
Pyrene	10	Protocol	125	[illegible]	0.05	ACN
Benzo(a)anthracene	10	Protocol	250	[illegible]	0.10	ACN
Chrysene	10	Protocol	250	[illegible]	[illegible]	ACN
Benzo(b)fluoranthene	1000	Protocol	[illegible]	[illegible]	[illegible]	ACN
Benzo(k)fluoranthene	1000	Protocol	[illegible]	[illegible]	[illegible]	ACN
Benzo(a)pyrene	1000	Protocol	[illegible]	[illegible]	[illegible]	ACN
Dibenzo(ah)anthracene	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	ACN
Benzo(ghi)perylene	[illegible]	[illegible]	[illegible]	[illegible]	2.0	ACN
p-Terphenyl	[illegible]	[illegible]	[illegible]	[illegible]	0.20	ACN
UV 254						
Acenaphthylene	[illegible]	[illegible]	250	25	10	ACN
Indeno(123cd)pyrene	[illegible]	[illegible]	100	25	4.0	ACN

Calibration Standards

GPL STD ID	Conc., ug/ml		Initial Amount,ul	Final Volume, ml	Final Conc. ug/ml	Solvent
GPL STD 5	0.05-8.0	WS	1000	1000	See Table 3	ACN
GPL STD 4	0.05-8.0	WS	750	1000	See Table 3	ACN
GPL STD 3	0.05-8.0	WS	500	1000	See Table 3	ACN
GPL STD 2	0.05-8.0	WS	250	1000	See Table 3	ACN
GPL STD 1	0.05-8.0	WS	100	1000	See Table 3	ACN

Table 3
Initial Calibration Concentrations

	Concentration, ug/ml				
Fluorescence	**CALSTD1**	**CALSTD2**	**CALSTD3**	**CALSTD4**	**CALSTD5**
Naphthalene	2.0	5.0	10	15	20.0
Acenaphthene	0.20	0.50	1.0	1.5	[illegible]
Fluorene	0.40	1.0	2.0	3.0	[illegible]
Phenanthrene	0.05	0.125	0.25	[illegible]	[illegible]
Anthracene	0.10	0.25	[illegible]	[illegible]	[illegible]
Fluoranthene	1.0	2.5	[illegible]	7.5	[illegible]
Pyrene	0.005	0.0125	[illegible]	0.0375	[illegible]
Benzo(a)anthracene	0.01	[illegible]	[illegible]	0.075	[illegible]
Chrysene	0.01	[illegible]	[illegible]	[illegible]	[illegible]
Benzo(b)fluoranthene	0.40	[illegible]	[illegible]	[illegible]	[illegible]
Benzo(k)fluoranthene	0.80	2.0	[illegible]	[illegible]	[illegible]
Benzo(a)pyrene	0.10	[illegible]	[illegible]	[illegible]	1.0
Dibenzo(ah)anthracene	0.20	[illegible]	[illegible]	[illegible]	2.0
Benzo(ghi)perylene	[illegible]	[illegible]	[illegible]	1.5	2.0
p-Terp d14	[illegible]	[illegible]	[illegible]	0.15	0.2
UV 254					
Acenaphthylene	[illegible]	2.5	5.0	7.5	10
Fluorene	[illegible]	1.0	2.0	3.0	4.0
Phenanthrene	[illegible]	0.125	0.25	0.375	0.5
Anthracene	[illegible]	0.25	0.5	0.75	1.0
Fluoranthene	[illegible]	2.5	5	7.5	10
Benzo(b)fluoranthene	[illegible]	1.0	2.0	3.0	4.0
Benzo(k)fluoranthene	0.80	2.0	4.0	6.0	8.0
Benzo(a)pyrene	0.10	0.25	0.5	0.75	1.0
Indeno(1,2,3-cd)pyrene	0.40	1.0	2.0	3.0	4.0

SOP No: N.7

Title: Soil Extraction for Pesticides/PCBs Compounds by Method 3550B (Sonication Extraction)

1.0 APPLICATION AND SCOPE

1.1 This method is a procedure for extracting organochlorine pesticides and PCB compounds from solids such as soils, sludges, and wastes. Extracts are suitable for analysis by methods 8081A and 8082.

1.2 Method 3550B describes both high level and low level extraction procedures. This SOP is based on the low level version of method 3550.

2.0 SUMMARY OF METHOD

2.1 A 30g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. Mixture is extracted with solvent three times using sonication. The extract is separated from the sample by filtration. The extract is ready for cleanup following concentration.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. These materials must be demonstrated to be free from interferences under the conditions of the analysis of analyzing method blanks.

4.0 APPARATUS AND MATERIALS

4.1 Mortar Model 155 Grinder, Fisher Scientific Company, or an equivalent brand and model

4.2 Ultrasonic cell disrupter, Heat Systems - Ultra Sonic, Inc., Model W-385 (475 watt) Sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" Tapped Disrupter Horn) plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard Tapped Microtip Probe (where applicable)

4.3 Pasteur Glass Pipets, Disposable, 1ml

4.4 Beakers, 400ml

4.5 Filtration Apparatus

- Conical funnel
- Filter paper: Whatman No. 41 or equivalent

4.6 Kuderna-Danish (K-D) Apparatus

4.6.1 Concentrator tube: 10ml graduated (Kontes K-570050-1025 or equivalent).

4.6.2 Evaporator Flask: 500ml (Kontes K-570001-0500 or equivalent).

4.6.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.7 Solvent extracted Boiling Chips, approximately 10/40 mesh (Silicon Carbide or equivalent).

4.8 Heated Water Bath, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.9 Top-loading Analytical Balance, capable of accurately weighing 0.01 grams.

4.10 12ml Vials and Caps

4.11 Glass Funnel

4.12 Nitrogen evaporation device equipped with a water bath that can be maintained at 35-40°C.

4.13 Spatula, Stainless steel or Teflon

4.14 Syringe, 1ml

4.15 Large disposable glass pipets

4.16 20ml scintillation vials with caps

5.0 REAGENTS

5.1 Sodium Sulfate: Anhydrous and reagent grade, heated at 400°C for 4 hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898, or equivalent.

5.2 Methylene chloride: acetone (1:1, V:V)

5.3 Methylene chloride (B&J GC2 grade or equivalent)

5.4 Hexane (pesticide quality or equivalent).

5.5 Concentrated sulfuric acid (reagent grade)

5.6 Florisil cartridges (0.5g packing B&J 9104 or equivalent)

6.0 PROCEDURE

6.1 Sample Handling and Storage

6.1.1 Samples are collected in appropriately sized glass bottles which have been precleaned and certified to be free of target analytes. Samples are shipped in coolers packed with ice and samples must be refrigerated at 2-6°C upon arrival. Holding time for soil samples is 14 days from the collection date. Samples must be brought to room temp before extraction begins. Spare containers if provided should be used for matrix spike and re-extractions (if needed).

6.1.2 Sediment/soil samples: Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

6.2 The following step should be performed to avoid loss of the more volatile extractables. Weigh approximately 30g of sample into a 400ml beaker. Record the weight to the nearest 0.01g. Add 1ml of surrogate standards to all samples, spikes, and blanks. For the sample in each analytical batch selected for spiking, add 1.0ml of the matrix spiking standard. The surrogates and spiking solutions must be added before any processing of the sample and QC begins. Nonporous or wet samples (gummy or clay type) lacking a free-flowing sandy texture must be mixed with 10-20g of anhydrous sodium sulfate using a spatula. The sample should be free-flowing at this point. Then immediately add 100ml of 1:1 methylene-chloride: acetone.

6.3 Sonicator tuning procedure

The sonicator is to be tuned weekly, at a minimum, and whenever any of the components are changed or, at the discretion of the analyst. The following procedure is to be followed for tuning.

6.3.1 Turn the power output knob to zero.

6.3.2 Turn the sonicator mode switch to continuous mode.

6.3.3 Turn the sonicator power switch on.

6.3.4 Press and hold the sonicator tune switch on with one hand for the Tekmar sonicator; use the other hand to turn the power output knob or the sonicator tuning knob as follows. For the Misonix sonicators, the tune switch will stay on by itself

6.3.5 Slowly turn the power output knob toward 10 while watching the output power meter reading. When the meter reading reaches 50%, turn the tuning knob until the minimum meter deflection is observed. The minimum deflection can be determined by observing when the needle starts to go back up when turning the tuning knob in either direction. The tuning knob for the Tekmar sonicator and the Misonix sonicators is on the front panel of the generator.

6.3.6 Proceed again with step (6.5.5.) until reaching output level 10 (output level 5 for microtips), and adjust the tuning knob to achieve the minimum deflection. At this point, the sonicator is considered tuned and operational provided that minimum deflection is achieved and the sonicator power output meter reads less than 25% at the minimum.

6.3.7 If the tuning criteria can't be met, check for loose cable connections or loose horn to converter connection and tighten as necessary. Retune. If the tuning criteria still can't be met, try replacing horn and converter with backup units. Retune. If the tuning criteria still can't be met, notify the supervisor immediately so that repairs and/or a loaner can be obtained. Place a sign on the sonicator stating "Out of order, do not use".

6.3.8 Release the sonicator tune switch, switch the sonicator mode switch to pulsed mode and switch the sonicator off.

6.3.9 Record the tuning in the appropriate sonicator maintenance logs and weekly checklist.

6.4 Place the bottom surface of the tip of the #207 3/4" disrupter horn about 1/2" below the surface of the solvent, but above the sediment layer.

6.5 Sonicate for 3 minutes with the output control knob set at 10 and the mode switch set on pulse and the percent-duty cycle knob set at 8-10. DO <u>NOT</u> use a microtip probe.

6.6 Decant and filter extracts through Whatman No. 41 filter paper using filtration or centrifuge and decant extraction solvent.

6.7 Repeat the extraction two more times with two additional 100ml portions of solvent. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the conical funnel and rinse with extraction solvent

6.8 Assemble a Kudema-Danish (K-D) Concentrator by attaching a 10ml concentrator tube to a 500ml evaporative flask.

6.9 Dry the extract by passing it through a drying funnel filled with anhydrous Sodium Sulfate. Collect the dried extract in a K-D Concentrator. Wash the extractor flask and Sodium Sulfate Column with 100-125ml of extraction solvent to complete the quantitative transfer.

6.10 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder Column. Pre-wet the Snyder Column by adding about 1ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (90-100°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 10ml, remove the K-D apparatus and add 50ml of Hexane through the top of Snyder column and continue concentration until liquid volume reaches about 5ml.

6.11 Remove the Snyder Column and rinse the flask and its lower joint into the concentrator tube with 1-2ml of Hexane. Adjust the volume of extract to 10.0ml with hexane and proceed with any cleanups, if required.

6.12 If PCB's only are to be quantitated, an acid cleanup may be done as follows: Transfer the 10mL extract into a 20mL scintillation vial, add 5mL concentrated sulfuric acid, cap tightly and shake vigorously for 2 minutes. Let the layers settle and centrifuge if necessary. If the extract (top layer) is still cloudy repeat the cleanup as many times as necessary by pipetting the extract into a clean vial and adding a fresh volume of acid. If extracts are to be used for separate pesticide and PCB analysis, split the extract by using 5mL for the acid cleanup and the remaining 5mL save for subsequent florisil cleanup, if needed.

6.13 If florisil cleanup is required, carefully homogenize the 10ml extract and take 1.0ml for cleanup.

6.13.1 Florisil cartridge cleanup

- Attach the vacuum manifold to a vacuum pump with a trap installed between the manifold and vacuum source. Place 1 florisil cartridge into vacuum manifold for each sample extract.

- Wash each cartridge with hexane/acetone (90:10) v:v. Pass at least 5ml of hexane/acetone solution through the cartridge while pulling a vacuum, adjust the vacuum so that the flowrate is approximately equal through each cartridge. DO NOT LET THE CARTRIDGES GO DRY AFTER THEY HAVE BEEN WASHED.

- After the cartridges have been washed, release the vacuum, and place a rack containing labeled 20ml vials inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is in the appropriate cartridge as the manifold top is replaced.

- Once the flasks are in place, restore vacuum to the manifold and place 1ml of the sample extract into the cartridge.

- Elute the cartridge with 8ml of hexane/acetone (90:10), then rinse the cartridge with two 1ml portions of hexane.

- Shut off the vacuum, take off the manifold top and remove the 20ml vials and place in the nitrogen blowdown manifold and blow the extract down to 1.0ml.

- Pipet the extract into labeled 1ml vials using a disposable pasteur pipe, taking care to rinse the sides of the 20ml vial with extract to ensure a quantitative transfer of extract. The 1ml vial is then transferred for GC analysis.

7.0 QUALITY CONTROL

7.1 Method Blank

7.1.1 A method blank is purified solid matrix (NA_2SO_4) for soil samples, carried through the entire extraction. The method blank weight must be approximately equal to the sample weights being processed.

7.1.2 Method blank extraction must be performed per each batch of 20 samples or less.

7.2 Matrix Spike/Matrix Spike Duplicate

7.2.1 Matrix Spike/Matrix Spike Duplicate frequency of extraction

Matrix spike and matrix spike duplicate extraction must be performed per each batch of 20 samples or less. If the batch of samples are received periodically, then MS/MSD are extracted every 14 days.

7.3 Matrix Spiking Solution is prepared in acetone and 1.0ml is added to the designated samples. The mixture contains the following compounds at the given concentrations:

Analyte	Conc.	Analyte	Conc.
4,4'-DDD	0.5PPM	Endosulfan II	0.5PPM
4,4'-DDE	0.5PPM	Endosulfan sulfate	0.5PPM
4,4'-DDT	0.5PPM	Endrin	0.5PPM

Aldrin	0.5PPM	Endrin Aldehyde	0.5PPM
Alpha-BHC	0.5PPM	Endrin Ketone	0.5PPM
Alpha-Chlordane	0.5PPM	Gamma-Chlordane	0.5PPM
Beta-BHC	0.5PPM	Heptachlor	0.5PPM
Delta BHC	0.5PPM	Heptachlor Epoxide	0.5PPM
Dieldrin	0.5PPM	Lindane (Gamma-BHC)	0.5PPM
Endosulfan I	0.5PPM	Methoxychlor	0.5PPM

Aroclors 1016 and 1260 are added when samples are extracted for PCBs only, at a concentration of 5.0ppm and 10.0ppm respectively.

7.4 Surrogate Spike

Each sample, matrix spike, matrix spike duplicate and blank is spiked with surrogate compounds prior to extraction. The concentration in the following table exhibits the concentration in the spiking solution.

Compounds	Concentration in ug/ml
Decachlorobiphenyl	1.0ml of 0.2ug/ml
TCMX	1.0ml of 0.2ug/ml

7.5 Lab Control Spikes (LCS)

Blank spikes are extracted at the same frequency as matrix spikes using Na_2SO_4 as the matrix. LCS spiking levels are the same as matrix spike concentrations. If only PCBs are needed LCS is spiked with AR1260 and AR1016 only. Aroclors LCS level are the same as matrix spike concentrations.

8.0 SAFETY

8.1 Safety glasses, lab coat, and gloves should be worn at all times during extraction.

8.2 Label reagents, spikes, surrogate solutions with solution type, concentration, date, chemist's initials and shelf life.

9.0 POLLUTION PREVENTION

9.1 GPL Laboratory operates in a safe manner to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. For more detail on pollution prevention, refer to GPL SOP D.5.

10.0 WASTE MANAGEMENT

10.1 Several wastes that GPL generates can be handled in a fairly routine manner. The process of describing the method for waste disposal of chemicals including standards and reagent solutions, and process waste, and samples is described in Standard Operating Procedures D.1 and D.2.

11.0 DEFINITIONS

11.1 For definitions of terms used in this document, refer to GPL Laboratory SOP G.14.

12.0 REFERENCES

12.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition.

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SOP No: N.6

Title: Method 3520C. Continuous Liquid-Liquid Extraction for Pesticides/PCBs

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics such as Organochlorine Pesticides and PCBs from water, wastewater, groundwater and TCLP extracts. Extracts produced by this method may be analyzed by Methods 8081A and 8082.

1.2 This method also describes concentration techniques suitable for preparing the extract for the appropriate method.

2.0 DEFINITIONS

2.1 For definitions of terms used in this document, refer to GPL Laboratory SOP G-14.

3.0 SUMMARY OF METHOD

3.1 A measured volume of sample, usually 1 liter, is placed into a continuous liquid-liquid extractor, adjusted, if necessary, to a specific pH and extracted with organic solvent for 18 ± 2 hours. The extract is dried, concentrated and exchanged into a solvent compatible with the step being employed.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifact and/or interferences to sample analysis. All materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

5.0 APPARATUS AND MATERIALS

- Continuous Liquid-Liquid Extractor (Equipped with joints and snapring clips)
- Drying Column (A glass funnel with pyrex glass wool at the neck of the funnel, half filled with dry Na_2SO_4)
- Kudema-Danish (K-D) Apparatus
  - Concentrator tube: 10ml, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.
  - Evaporator flask: 500ml (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.
  - Snyder column: Three-ball macro (Kontes K-569000-0121 or equivalent)
- Solvent extracted Boiling Chips, approximately 10/40 mesh silicon carbide or equivalent)
- Heated water Bath, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.
- Glass vials, 2 ml capacity, with Teflon-lined crimp cap
- pH Indicator Paper covering pH 2 to pH 12
- Rheostat controlled Heating Mantle
- 10ml Gas-Tight Syringe
- One 1 Liter Class A Graduated Cylinder
- Pyrex Glass Wool
- 1g florisil cartridge
- Large disposable glass pipets

6.0 REAGENTS

- Reagent Water (water in which an interferant is not observed at the method detection limit of the compounds of interest).
- Sodium Hydroxide Solution, 10N

  (ACS) Dissolve 40g NaOH in reagent water and dilute to 100ml.

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- Sodium Sulfate
  (ACS) Granular, Anhydrous (purified by heating at 400°C for 4 hours in a shallow tray)

- Sulfuric Acid Solution (1:1)
  Slowly add 50ml of H_2SO_4 (sp. gr. 1.84) to 50ml of reagent water.

- Methylene Chloride (B & J GC2 grade or equivalent)

- Hexane (Pesticide grade)

- Acetone (pesticide grade)

7.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

7.1 Samples are collected in 1 liter amber glass bottles which have been precleaned and certified to be free of target analytes. Samples are shipped in coolers packed in ice and stored at the lab in refrigerators at 2-6°C until extraction. The holding time for extraction is 7 days from sample collection.

8.0 PROCEDURE

8.1 Place a few boiling stones in a 500ml collection flask and assemble continuous extractor.

8.2 Add 50ml of methylene chloride to the extractor.

8.3 Using a Class A graduated cylinder, measure out 1 liter of sample and transfer it to the continuous extractor. Rinse the sample bottle with 20-30ml methylene chloride and add to the extractor. Add 1.0ml of surrogate spiking solution. Check the pH of the sample using wide range pH paper and adjust the pH to 7 using 1:1 H_2SO_4 or 10N NaOH. Use 1.0 liter of deionized water to another extractor for the method blank preparation and analysis.

8.4 For the sample in each analytical batch selected for spiking, measure two additional 1.0 liter aliquots. Add 1.0ml of the matrix spiking standard.

8.5 Add sufficient methylene chloride to the extractor to ensure proper operation and extraction for 18 ± 2 hours.

8.6 Allow to cool, then detach and label the boiling flask. The extract is then ready to be dried and concentrated.

8.7 Assemble a Kuderna-Danish (K-D) Concentrator by attaching a 10ml concentrator tube to a 500ml evaporation flask.

8.8 Dry the extract by passing it through a drying column containing about 10cm anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the flask which contained the solvent extract with 20-30ml of methylene chloride and add to the column to complete the quantitative transfer.

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8.9 Add one or two clean boiling chips to the flask and attach a three ball Snyder Column. Pre-wet the Snyder Column by adding approximately 1ml of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (90-100°C) until the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration. When the apparent volume of liquid reaches about 10ml, remove the K-D apparatus from the water bath and perform a solvent exchange by adding 50ml of hexane through the top of Snyder column. Continue concentration in the water bath until the volume of extract reaches approximately 5ml

8.10 Take the K-D off the water bath and place on a rack and allow to cool. Disconnect the concentrator tube and adjust the volume to 10.0ml with hexane.

8.11 If florisil cleanup is required, carefully homogenize the 10ml extract and take 1.0ml for cleanup.

8.11.1 Florisil cartridge cleanup:

- Attach the vacuum manifold to a vacuum pump with a trap installed between the manifold and vacuum source. Place 1 florisil cartridge into vacuum manifold for each sample extract.

- Wash each cartridge with hexane/acetone (90:10) v:v. Pass at least 5ml of hexane/acetone solution through the cartridge while pulling a vacuum; adjust the vacuum so that the flow rate is approximately equal through each cartridge. DO NOT LET THE CARTRIDGES GO DRY AFTER THEY HAVE BEEN WASHED.

- After the cartridges have been washed, release the vacuum, and place a rack containing labeled 20ml vials inside the manifold. Care must be taken to ensure that the solvent line from each cartridge is in the appropriate cartridge as the manifold top is replaced.

- Once the flasks are in place, restore vacuum to the manifold and place 1ml of the sample extract into the cartridge.

- Elute the cartridge with 8ml of hexane/acetone (90:10), then rinse the cartridge with two 1ml portions of hexane.

- Shut off the vacuum, take off the manifold top and remove the 20ml vials and place in the nitrogen blowdown manifold and blow the extract down to 1.0ml.

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- Pipet the extract into labeled 1ml vials using a disposable pasteur pipet, taking care to rinse the sides of the 20ml vial with extract to ensure a quantitative transfer of extract. The 1ml vial is then transferred for GC analysis.

9.0 QUALITY CONTROL

9.1 Method Blank

9.1.1 The method blank is a volume of deionized, laboratory water carried through the entire extraction. The method blank volume must be equal to 1.0 liter or the sample volumes being extracted.

9.1.2 Frequency of Method Blanks
Method blank extraction must be performed per each batch of samples, not to exceed 20 samples per batch.

9.2 Matrix Spike/Matrix Spike Duplicate

9.2.1 MS/MSD Frequency of Extraction

Matrix spike and matrix spike duplicate extraction must be performed per each batch of 20 samples or less. If the batch of samples are received periodically, then MS/MSD are extracted every 14 days.

9.3 Matrix Spiking Solutions

9.3.1 Method 8081A matrix spikes

Matrix spike is prepared in acetone and 1.0ml is added to the designated samples. The mixture contains the following compounds at the given concentrations

4,4'-DDD	0.5ppm
4,4'-DDE	0.5ppm
4,4'-DDT	0.5ppm
Aldrin	0.5ppm
Alpha-BHC	0.5ppm
Alpha-Chlordane	0.5ppm
Beta-BHC	0.5ppm
Delta-BHC	0.5ppm
Dieldrin	0.5ppm
Endosulfan I	0.5ppm
Endosulfan II	0.5ppm
Endosulfan Sulfate	0.5ppm
Endrin	0.5ppm
Endrin Aldehyde	0.5ppm
Endrin Ketone	0.5ppm
Gamma-Chlordane	0.5ppm
Heptachlor	0.5ppm

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Heptachlor Epoxide	0.5ppm
Lindane (Gamma-BHC)	0.5ppm
Methoxychlor	0.5ppm

LCS spiking levels are the same as those used to spike samples.

9.4 Surrogate Spike (SS)

Each sample, matrix spike, and blank are spiked with surrogate compounds prior to extraction. The concentration in the following table exhibits the concentration in the spiking solution.

Compounds	Concentration Added
Decachlorobiphenyl	1.0ml of 0.2ug/ml
TCMX	1.0ml of 0.2ug/ml

9.5 Lab Control Spike (LCS)

Blank spikes are extracted at the same frequency as matrix spikes using deionized water as the matrix.

9.6 PCBs Spike (Method 8082)

When PCBs are only needed, follow the same extraction procedure as Pest/PCBs. For matrix spike and LCS QC runs use 1.0ml of AR1260 and AR1016 spiking solution of the concentration of 10.0 and 5.0ug/ml, respectively.

10.0 SAFETY

10.1 Safety glasses, lab coat, and gloves should be worn at all times during extraction.

10.2 Label reagents, spikes, surrogate solutions by identifying the solution, concentration, date, chemist's initials, and shelf life.

10.3 Waste Disposal

10.3.1 Chlorinated solvent waste should be put into a polyethylene safety can designated for methylene chloride. This will be disposed of by the hazardous waste coordinator.

10.3.2 Water waste can be poured down the drain after neutralizing it using H_2SO_4 or NaOH depending upon the pH of the waste.

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11.0 WASTE MANAGEMENT

11.1 Several wastes that GPL generates can be handled in a fairly routine manner. The process of describing the method for waste disposal of chemicals including standards and reagent solutions, and process waste, and samples is described in Standard Operating Procedure D.1 and D.2.

12.0 POLLUTION PREVENTION

12.1 GPL Laboratory operates in a safe manner to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. For more detail on pollution prevention, refer to GPL SOP D.5.

13.0 REFERENCES

- Test Methods For Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition.

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SOP No: Q.7

Title: SOP for Method 8082
Aroclor and PCB Congeners

1.0 SCOPE AND APPLICATION

1.1 Method 8082 is used to determine the concentrations of various polychlorinated biphenyls (PCBs) as Aroclors or as individual PCB congeners in various matrices such as aqueous, solids, oils, products and wipes. Table 1 indicates compounds that may be determined by this method.

TABLE 1

Target Compounds
2-Chlorobiphenyl
2,3-Dichlorobiphenyl
2,2',5-Trichlorobiphenyl
2,4',5-Trichlorobiphenyl
2,2',5,5'-Tetrachlorobiphenyl
2,3',4,4'-Tetrachlorobiphenyl
2,2',3,4,5'-Pentachlorobiphenyl
2,2',4,5,5'-Pentachlorobiphenyl
2,3,3',4',6-Pentachlorobiphenyl
2,2',3,4,4',5'-Hexachlorobiphenyl
2,2',3,4,5,5'-Hexachlorobiphenyl
2,2',3,5,5',6-Hexachlorobiphenyl
2,2',4,4',5,5'-Hexachlorobiphenyl
2,2',3,3',4,4',5-Heptachlorobiphenyl
2,2',3,4,4',5,5'-Heptachlorobiphenyl
2,2',3,4,4',5',6-Heptachlorobiphenyl
2,2',3,4',5,5',6-Heptachlorobiphenyl
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
Aroclor 1016
Aroclor 1260
Aroclor 1221
Aroclor 1232
Aroclor 1242
Aroclor 1248

Aroclor 1254
Tetrachloro-m-xylene(Sur)
Decachlorobiphenyl (Sur)

2.0 SUMMARY OF METHOD

2.1 Method 8082 provides gas chromatographic conditions for the detection of ppb levels of certain polychlorinated biphenyls and congeners.

Prior to the use of this method, appropriate sample extraction techniques must be used

3.0 INTERFERENCES

3.1 Interferences by phthalate esters can pose a major problem in PCB determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large-eluting peaks, especially in the 15% and 50% fraction from cleanups. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatograph

Hewlett Packard GC Systems 5890 equipped with autosampler is used. EnviroQuant software systems for data recording and processing is interfaced with the GC system

4.2 Columns

4.2.1 Dual column connected with a "Y" connector to a single injection port is used In this mode, material injected is split between the columns and detected by 2 separate ECD detectors.

4.2.2 Column 1: 30 meter, 5% opphenyl DI Methyl Polysiloxane (RTX-CLP) fused silica column is used.

4.2.3 Column 2: 30 meter, 14% cyanopropyl methyl polysiloxane (RTX-CLP2) fused silica column is used.

4.2.4 5 meter guard column (inert) is used at the "Y" connector.

4.3 GC Condition

4.3.1 The following GC parameters are implemented when PCBs are analyzed:

- Injection port temperature 200°C
- Detectors temperature 300°C
- A double ramp temperature program is used

1st Ramp:	
Initial temperature	150°C
Initial time	1.0 min
Rate	15°C/min
Final temperature	200°C
Final time	4.0 min

2nd Ramp:	
Initial temperature	200°C
Rate	10°C/min
Final temperature	300°C
Final time	5.0 min

- Equilibrium time 0.75 min
- Septum purge on at 0.75 min at about 2ml/min
- Attenuation 0
- Signal rages 0
- Splitless purge 50ml/min
- Makeup gas 80ml/min

4.3.2 The following GC parameters are implemented when PCTs are analyzed:

Injector Temp	200°C
Detector Temp	300°C
Initial Temp	150°C
Initial Time	1.0 min.
Ramp Rate	15°/min.
Final Temp	300°C
Final Time	15 min.

The Electronic Pressure Controller should be programmed as follows:

Initial Pressure Time	20min.
Initial Pressure	8 PSI
Rate	99 PSI
Final Pressure	25 PSI
Final Time	13min.

4.4 Gases

4.4.1 Helium ultrapure grade is used as a gas carrier at about 5ml per min at 50° measured at the column end.

4.4.2 Make up gas is Argon/Methane (5% methane) and the flow rate is about 80 ± 5ml per min for each detector.

5.0 CALIBRATION AND STANDARDIZATION

Calibration standards are prepared at five concentration levels through dilution of the stock standards with hexane (refer to standard logbook). Concentrations of the five level calibration and single point Aroclor are listed on Table 2.

5.1 Aroclors

To demonstrate the linearity of the detector, a five point concentration of a mixture of Aroclor 1016 and Aroclor 1260 should be analyzed. Mid-level point of other five Aroclor (listed in Table 1) are required to aid in pattern recognition and single point calibration

5.2 PCB Congeners

If samples are to be determined for individual PCB congeners, prepare a minimum of five concentrations of PCB congeners.

TABLE 2

Compound	Level 1 (ug/L)	Level 2 (ug/L)	Level 3 (ug/L)	Level 4 (ug/L)	Level 5 (ug/L)
2-Chlorobiphenyl	5	25	50	75	100
2,3-Dichlorobiphenyl	5	25	50	75	100
2,2',5-Trichlorobiphenyl	5	25	50	75	100
2,4',5-Trichlorobiphenyl	5	25	50	75	100
2,2',3,5'-Tetrachlorobiphenyl	5	25	50	75	100
2,2',5,5'-Tetrachlorobiphenyl	5	25	50	75	100
2,3',4,4'-Tetrachlorobiphenyl	5	25	50	75	100
2,2',3,4,5'-Pentachlorobiphenyl	5	25	50	75	100
2,2',4,5,5'-Pentachlorobiphenyl	5	25	50	75	100
2,3,3',4',6-Pentachlorobiphenyl	5	25	50	75	100
2,2',3,4,4',5'-Hexachlorobiphenyl	5	25	50	75	100
2,2',3,4,5,5'-Hexachlorobiphenyl	5	25	50	75	100
2,2',3,5,5',6-Hexachlorobiphenyl	5	25	50	75	100
2,2',4,4',5,5'-Hexachlorobiphenyl	5	25	50	75	100
2,2',3,3',4,4',5-Heptachlorobiphenyl	5	25	50	75	100
2,2',3, 4,4',5,5'-Heptachlorobiphenyl	5	25	50	75	100
2,2',3,4,4',5',6-Heptachlorobiphenyl	5	25	50	75	100
2,2',3,4',5,5',6-Heptachlorobiphenyl	5	25	50	75	100
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	5	25	50	75	100
AR1016	100	250	500	750	1000
AR1221			500		
AR1232			500		
AR1242			500		
AR1248			500		
AR1254			500		
AR1260	200	500	1000	1500	2000
Tetrachloro-m-xylene	5	12.5	25.0	37.5	50.0
Decachlorobiphenyl	5	12.5	25.0	37.5	50.0

5.3 Surrogates. Tetrachloro-m-xylene and Decachlorobiphenyl are used in PCB analyses. Calibration levels are indicated on Table 2.

5.4 Calibration

If samples are to be analyzed for Aloclor.

5.4.1 Five-level calibration of a mixture of Aroclor 1016 and Aroclor 1260 are initially analyzed. Percent RSD (Relative Standard Deviation) must be ≤20% for the Aroclors except surrogates. Analysis of single point mid level concentration of other five Aroclor listed in Table 1 are required. If PCB's are detected in the sample, patterns are compared for fingerprint match with initial standards and corresponding PCB's and retention time. Calculation is based on average area quantification of five representative peaks. When interferences are present, those peaks with less interferences may be chosen for quantification. Fewer peaks (minimum of 3 peaks) may be used for quantitation if there are considerable interferences.

5.4.2 Daily continuing calibration: Analyst should alternate the use of high and low concentrations of Aroclor 1016 and Aroclor 1260 at the beginning of each shift. Percent difference should be kept at ±5% for the Aroclors except for surrogates. If this criteria is exceeded for any Aroclor, calculate the average percent difference for all analytes in the calibration. And if the calculated average response factor for all analyte is within 15%, then the calibration is considered valid.

5.4.3 Mid sequence standard: mid-level mixture of Aroclor 1016/1260 should be injected every ten injections of samples and/or QC and at the end of every 12 hours, whichever is more frequent. All samples that were injected after the standard exceed the criteria of linearity must be re-injected if analyses indicate the presence of specific target analyte. However, if continuing calibration is ≥15% and no target analyte was detected, re-injection of the samples is not necessary. If continuing calibration ≤15% and no target analyte was detected, re-injection is necessary. Experience of the chromatographer is an influential factor in the determination of sample reanalysis.

If samples are to be analyzed for congeners.

5.4.4 Initially five point calibration of 19 congeners are analyzed. The mean of the RSD value for all congeners must be equal or less than 20%. The initial calibration must be verified at the beginning of each 12-hour analytical shift during which samples are analyzed. A calibration standard must also be injected at the interval of 10 samples or/and QC samples, and at the end of the analysis sequence.

$$\% \text{ Difference} = \frac{CF_I - CF}{CF_I} * 100$$

Where:

CF_I = mean calibration factor from the initial calibration
CF = calibration factor from calibration verification standard

The calibration factor for each analyte calculated must not exceed a difference of more than 15% when compared to the mean calibration factor from the initial calibration. When calibration verification standard failed to meet the QC criteria, all samples that were injected after the last standard that met the QC criteria must be re-injected. However, if the sensitivity of the instrument had increase and target compounds are not present in the sample, there is no need for re-analysis.

6.0 SAMPLE COLLECTION, HANDLING, PRESERVATION AND HOLDING TIMES

6.1 Sample extracts are preserved by keeping them cooled to 4°C.

6.2 The holding times for extraction of the samples are 7 days of sampling for water samples and 14 days of sampling for soil samples. If sample has been extracted outside the holding time, note the aberration on the sample non-conformity report, and notify the manager for further instruction.

6.3 Sample must be analyzed within 40 days of the extraction. If sample has been analyzed outside the holding time, note the aberration on the sample non-conformity report, and notify the manager.

7.0 METHOD DETECTION LIMITS

7.1 Method detection limits for this method are listed in the GPL Laboratory Method Detection Limit and Reporting Limit official book.

8.0 METHOD PERFORMANCE

8.1 The MDL concentrations listed in the GPL MDL book are generally obtained using organic-free reagent water. Results were also obtained by extracting seven spiked replicates the same way as the samples and analyzing them. MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. Precision and accuracy studies are performed once a year at a minimum. Single operator precision, overall precision and method accuracy were found to be directly related to the concentration of the parameter.

9.0 PROCEDURE

9.1 Retention time windows

9.1.1 Make 3 injections of all single component standard mixtures throughout the course of a 72-hour period. Calculate standard deviation of the three absolute retention times for each single component standard. For multi-response products, choose one major peak from the cluster and calculate the standard deviation of the three retention times for that peak.

9 1 1 1 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define retention time window For multipeak products, primarily combination of chromatography pattern and retention times are used.

9 1 1 2 In those cases where the standard deviation for a particular standard is zero, substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

9 1 1 3 When a new GC column is installed retention time window must be established.

9.2 Sample Preparation

For sample preparation of soil and water, refer to GPL SOPs N.6 and N.7.

9.3 When all calibration requirements are met sample analysis may begin. After each batch of 10 runs linearity should be checked before any more samples are analyzed All samples that were injected after the standard exceeding the criteria must be re-injected, if the initial analysis indicates the presence of a specific Aroclor that exceeded the criteria.

9.4 Dilution must be made if the response exceed the linear range of the compounds

9.5 Peak identification is based on detection on <u>both</u> columns. A daily retention time window is established for each analyte from section 5.1 as the midpoint of the window for that day The daily retention time window equals the midpoint ± 3 times the standard deviation determined in section 6.1.

9.6 GCMS Confirmation may be implemented if the concentration permits.

9.7 Wipe samples are treated like a solid sample and results are reported as ug per wipe. All QC parameters used for soil samples are applicable to wipes except for MS/MSD analysis An actual MS/MSD analysis is impractical since only one wipe is sampled at a location and it can not be split.

9.8 If peak detection and pattern identification are prevented by interferences, the extract should undergo acid cleanup using Method 3665A or sulfur cleanup using Method 3660B. The experience of the analyst may prove invaluable in determining which cleanup method is appropriate for particular samples.

10.0 DATA ANALYSIS AND CALCULATIONS

10.1 All quantifications are based on external standard calculations.

10.1.1 Calculation for calibration factor

$$\text{Calibration factor} = \frac{\text{Total Average Area of Peak*}}{\text{Mass injected (nanograms)}}$$

* for multipeak analytes use total areas of all designated peaks for quantitation

10.1.2 Percent Difference

$$\text{Percent difference} = \frac{(R_1 - R_2)}{R_1} \times 100$$

R_1 = Calibration factor from first analysis
R_2 = Calibration factor from succeeding analyses

10.1.3 The concentration of each Aroclor in the sample may be determined by calculating the amount of standard injected from the peak response, using the calibration factor determined from the initial five point calibration for Aroclor 1016 and for 1260. For other Aroclor that may be present in the sample, CF from the single point calibration standard of the specific Aroclor will be used for calculation.

Aqueous Concentration (ug/L) = $[(A_x)(A)(Vt)(D)]/[(As)(Vi)(Vs)]$

Solid Concentration (ug/kg) = $[(A_x)(D)(A)(V_t)]/[(As)(Ws)(Vi)]$

where:

A_x = Response for the analyte in the sample, (area or peak height
A = Amount of standard injected in ng
As = Response for the external standard
Vi = Volume of extract injected
D = Dilution factor, if any
Vt = Volume of total extract
Vs = Volume of sample extracted
s = Weight of sample extracted

- For non-aqueous samples, the unit is µg/kg and dry weight of sample is used for Ws.

11.0 QUALITY CONTROL

11.1 Required Instrument QC

11.1.1 Percent RSD should be ≤20% when 5 point calibration factors are compared.

11.1.2 Percent difference of daily response of a given analyte should be within ±15% when compared to initial responses.

11.1.3 All succeeding standards in an analysis sequence must fall within daily retention time window established by the first standard of the sequence.

11.1.4 Control limits for MS/MSD, LCS, surrogates are established and published yearly for internal use.

11.2 Matrix Spikes

11.2.1 For each analytical batch of up to 20 samples MS and MSD must be analyzed. If less than twenty samples are analyzed per month, MS/MSD must be analyzed on per month basis. Percent recoveries and Relative Percent Difference (RPD) should be calculated as follows:

$$\text{Matrix Spike \% Recovery} = \frac{SSR-SR}{SA} \times 100$$

where:

SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added from Spiking Mix

$$RPD = \frac{D1 - D2}{(D1 + D2)/2} \times 100$$

D1 = First Sample Value
D2 = Second Sample Value

If samples are analyzed for PCBs only, then matrix spikes must be analyzed for AR1016 and AR1260.

11.3 Lab Control Sample (LCS)

11.3.1 A control check sample is extracted and analyzed at frequency similar to MS/MSD with each extracted batch. Lab Control Spikes (LCS) are analyzed per batch or every 20 samples, whichever comes first. LCS compound must be within the in-house established control limit. Statistical control limit are based on 20 data points. Data points used in the data set must not be selectively included or excluded. If recovery of LCS compound falls outside the established limit, corrective action must be taken. After corrective action, if LCS analyte recovery is still outside QC acceptance limits, all the associated samples batch must be re-extracted if holding times have not elapsed. When PCB analysis is needed the control check sample should be spiked with AR1016 and 1260 at the same levels as matrix spikes.

11.4 Blanks

11.4.1 Blank is extracted and analyzed with each analytical batch. Blanks must be contaminant free. Concentration of any confirmed peak should be less than the detection limit.

11.5 Surrogates

11.5.1 Percent recoveries for the surrogates are periodically (minimum of once a year) determined by plotting percent recoveries of surrogates measured in 20 consecutive blanks. Control limits for each surrogate compound is measured using the following formula:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

where p is the mean recovery and s is the standard deviation.

11.5.2 Two surrogate (TCMX and DCB) are added to each sample, however, only one need to be calculated for recovery. Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if the recovery is within limits. If recovery is not within limit, re-extract and reanalyze the sample.

12.0 SAFETY

12.1 Safety glasses for eye protection, laboratory coasts for body protection, latex gloves for hand protection.

12.2 Due to the toxicity or carcinogenicity of each reagent, each chemical compound should be treated as a potential health hazard.

12.3 Material Safety Data Sheets (MSDS) can be found on the procurement bookshelves located in the company library.

12.4 Preparation of the standard should be handled under a hood.

13.0 POLLUTION PREVENTION

13.1 GPL Laboratory operates in a safe manner to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. For more detail on pollution prevention, refer to GPL SOP D.5.

14.0 WASTE MANAGEMENT

14.1 Several wastes that GPL generates can be handled in a fairly routine manner. The process of describing the method for waste disposal of chemicals including standards and reagent solutions, and process waste, and samples is described in Standard Operating Procedures D.1 and D.2.

15.0 DEFINITIONS

15.1 For definitions of terms used in this document, refer to GPL Laboratory SOP G.14.

16.0 REFERENCES

- Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition

SOP No: S.1

Title: HPLC Analysis of Nitroaromatic and Nitramine Explosive Residues in Water, Soil, and Sediment Samples

Scope: This SOP describes the analytical methodology employed in the analysis of water, soil, and sediment extracts for explosive residues by Method 8330

1.0 METHOD SUMMARY

1.1 The purpose of this Standard Operating Procedure is to describe in detail the methodology used in the analysis of water, soil, and sediment extracts for explosive residue compounds. The methodology conforms to that specified in SW846 method 8330. The compounds to be analyzed in this method are listed in Table I.

TABLE I

COMPOUND NAME	CAS NO.
HMX	2691-41-0
1,3,5-TNB	99-35-4
Tetryl	479-45-8
TNT	118-96-7
4-ADNT	1946-51-0
2,6-DNT	606-20-2
4- Nitrotoluene	99-99-0
RDX	121-82-4
1,3-DNB	99-65-0
Nitrobenzene	98-95-3
2-ADNT	355-72-78-2
2,4-DNT	121-14-2
2-Nitrotoluene	88-72-2
3-Nitrotoluene	99-08-1
*PETN	78-11-5
*Nitroglycerine	55-63-0
*Picric Acid	88-89-1
*Diazodinitrophenol (DDNP)	

*Same Extract used but analyzed on different calibration parameters

2.0 REFERENCES

- SW846 Method 8330 revision 0 September 1994.

3.0 INTERFERENCES

3.1 Glassware and other sample processing hardware must be clean to minimize interferences.

3.2 2,4-DNT and 2,6-DNT elute at similar retention time (difference of 0.2 minutes). A large concentration of one isomer may mask the response of the other isomers. If it is not apparent that both samples are present, an isomeric mixture should be reported

3.3 Degradation product of tetryl appear as a shoulder on the 2,4,6-TNT peak. Peak height rather than peak area should be used when tetryl is present in the sample concentrations that are significant relative to the concentration of 2,4,6-TNT.

4.0 APPARATUS AND MATERIAL

4.1 HPLC Instrument

A Waters Model 501 Solvent Delivery System (HPLC Pump), Waters WISP 712 Autosampler and Waters Variable Wavelength Detector Model #486 or LINEAR UVIS-201 absorbance detector is used as an analytical system complete with primary column LC-18 (4.6mm by 25cm) particle size 5um, confirmatory column LC-CN (4.6mm by 25cm) particle size 5um and pre-column Waters HPLC inserts (uBondapak C18/GuardPak).

5.0 OPERATING PARAMETERS

- Mobile Phase: 50% HPLC grade Methanol to 50% deionized H2O.
- Flow Rate: 1.0ml/min for primary and confirmatory analysis.
- Injection volume 100ul fixed loop.
- Wavelength. 254 for all 8330 target compounds in Table 1.
- Mobile phase for CN column: 65% H_2O, 12% M_eOH and 23% Acetonitrile

6.0 REAGENTS AND STANDARDS

- HPLC Grade methanol and Acetonitrile
- Calcium Chloride Desiccant (High Purity)
- .45 um PTFE filters
- Neat standards of each compound in Table I acquired through U.S. Army, Environmental Center or Radian Cor. Standards
- Sodium Chloride, NaCl, Reagent Grade
- Tetrabutylammonium dihydrogen phosphate, 97%

7.0 SAMPLE COLLECTION, HANDLING AND HOLDING TIMES

7.1 Water samples may be collected in 1L or (quart) amber glass container. Soil samples may be collected in glass containers or closed end tubes.

7.2 All samples must be iced or refrigerated at 4°C (± 2°C) from the time of collection until extraction.

7.3 Extraction holding times for water is seven days from the date sampled and fourteen days from the date sampled for soil. Analysis holding times are 40 days from the date of extraction for both soil and water samples.

8.0 CALIBRATION AND STANDARDIZATION

8.1 Tables II and III indicate the calibration levels for the standard 8330 method. Two mixes are used because of the close proximity of the retention times for certain compounds.

8.2 Tables IV, V, VI, and VII indicate the calibration levels for PETN, Nitroglycerine, Picric Acid and Diazodinitrophenol (DDNP), respectively. The same sample extract may be used but separate calibrations are required because of the differences in the operating parameters.

TABLE II

COMPOUNDS (MIX A)	1st LEVEL (ppb)	2nd LEVEL (ppb)	3rd LEVEL (ppb)	4th LEVEL (ppb)	5th LEVEL (ppb)	6th LEVEL (ppb)
HMX	20	100	500	1000	2000	5000
*4-Nitroanaline	20	100	500	1000	2000	5000
1,3,5-TNB	10	50	250	500	1000	2500
Tetryl	20	100	500	1000	2000	[illegible]
TNT	10	50	250	500	1000	[illegible]
4-ADNT	10	50	250	500	1000	[illegible]
2,6-DNT	10	50	250	500	1000	[illegible]
4-Nitrotoluene	20	100	500	1000	2000	[illegible]

*Surrogate

TABLE III

COMPOUNDS (MIX B)	1st LEVEL (ppb)	2nd LEVEL (ppb)	3rd LEVEL (ppb)	4th LEVEL (ppb)	5th LEVEL (ppb)	6th LEVEL (ppb)
*4-Nitroaniline	20	100	500	1000	2000	5000
RDX	20	100	500	1000	2000	5000
1,3-DNB	10	50	250	500	1000	2500
Nitrobenzene	10	50	250	500	1000	2500
2-ADNT	10	50	250	500	1000	2500
2,4-DNT	10	50	250	500	1000	2500
2-Nitrotoluene	20	100	500	1000	2000	5000
3-Nitrotoluene	20	100	500	1000	2000	5000

*Surrogate

TABLE IV

COMPOUNDS	1st LEVEL (ppb)	2nd LEVEL (ppb)	3rd LEVEL (ppb)	4th LEVEL (ppb)	5th LEVEL (ppb)
*4-Nitroaniline	50	100	200	500	1000
PETN	50	100	200	500	1000

*Surrogate

TABLE V

COMPOUNDS	1st LEVEL (ppm)	2nd LEVEL (ppm)	3rd LEVEL (ppm)	4th LEVEL (ppm)	5th LEVEL (ppm)
Nitroglycerine	1	5	10	20	50

TABLE VI

COMPOUNDS	1st LEVEL (ppb)	2nd LEVEL (ppb)	3rd LEVEL (ppb)	4th LEVEL (ppb)	5th LEVEL (ppb)
Picric Acid	[illegible]	500	1000	1500	5000

TABLE VII

COMPOUNDS	1st LEVEL (ppb)	2nd LEVEL (ppb)	3rd LEVEL (ppb)	4th LEVEL (ppb)	5th LEVEL (ppb)
DDNP	50	250	1000	2000	5000

8.3 Initial Calibration is performed by analyzing six calibration levels (five levels for Nitroglycerin, PETN and picric acid). Percent RSD (Relative Standard Deviation) must be below 20% for the 6 points, (5 points for Ng, PETN and picric acid. Calculate response factor (RF) for each level of standard using peak area. Peak heights will be used to calculate the response factors if it is required by specific project

$$\%RSD \quad \frac{\text{Standard Deviation}}{\text{Average RF}} \times 100$$

$$RF(\text{Each Level}) \quad \frac{\text{Peak Area/Height of Analyte}}{\text{Concentration}}$$

8.3.1 Prior to use for sample analysis, the acceptability of the initial calibration curve must be verified through analysis of calibration verification (ICV) solutions obtained from a second source. Calibration verification analysis should meet the same acceptance criteria used for initial calibration.

8.4 A continuing Calibration is performed at the beginning of each shift by analyzing a high or low level concentration standard. The calibration difference must be below 15%

If this criteria is exceeded for any single component analyte, calculate the average percent difference across all analytes in the calibration. The calculated average percent difference across all analytes should be within ± 15%, to consider a valid calibration. This approach should be used only when limited number of poor performing compounds exceeded the 20% RSD but inside the 40% established limit. When this approach is used the data user should be aware that the use of this approach might lead to greater uncertainty for those analytes for which RSD is greater than 15%. The laboratory should communicate the following information within the case narrative to the client:

- Summary of all target analytes exceeding method acceptance criteria
- The individual RSD results for those compounds
- The mean RSD calculated

When a Continuing Calibration is passed, the calibration is acceptable for a 12 hour period starting from the beginning of the injection of the first standard. By alternating low and high concentration calibration of both MIX A and MIX B plus other required explosive standards are run every ten samples and a closing standard is run at the end of the batch or 24 hour period, whichever comes first. Closing standard must have a %D below 15. If the instrument does not meet the acceptance criteria a new initial calibration must be constructed. A new initial calibration is also required if a column is replaced or major instrument maintenance like changing the lamp or pump is replaced. Also, after corrective action, if the absolute retention time of the daily calibration is not within the established retention time window, a new initial calibration must be constructed. Minor corrective action like changing pre-column filter or washing column and

lines with pure methanol may not require performing a new initial calibration, provided the daily calibration that originally failed, now passes the acceptance criteria.

$$\% \text{ Difference} \quad \frac{RF_c - RF_i}{RF_i} \times 100$$

where:

RF_i Mean response factor from the most recent initial calibration

RF_c Response factor from continuing calibration

9.0 METHOD DETECTION LIMIT

9.1 Method detection limits for this method are listed in the GPL Laboratory Method Detection Limit and Reporting Limit official book.

10.0 METHOD PERFORMANCE

10.1 The MDL calculations listed in the GPL MDL book are generally obtained using digital reagent water. Results were also obtained by extracting seven spiked replicates the same way as the samples and analyzing them. MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. Precision and accuracy studies are performed once a year at a minimum. Single operator precision, overall precision and method accuracy were found to be directly related to the concentration of the parameter.

11.0 PROCEDURE

11.1 Aqueous Samples

11.1.1 Place 770ml aliquots of the aqueous sample, blank and blank matrix spike, in 1000ml erlenmeyer flasks. Add 1.00ml of 6ppm surrogate to each sample and 1.0ml of matrix spike to each LCS and sample matrix spike. Matrix spike solution, and surrogate solution prepared in methanol at 6 and 3ug/ml concentration using all target compounds.

11.1.2 Add 251.3g of NaCl plus a magnetic stir bar in to the flask and stir the sample using a magnetic stirrer, starting from medium to high speed until all of the NaCl is completely dissolved. Be sure to dissolve all salt before adding acetonitrile, or the dissolution process takes much longer.

11.1.3 Add a 164ml volume of acetonitrile using a glass erlenmeyer cylinder to each sample and stir on high speed for 20 minutes. Let the phases separate for about 10 minutes.

11.1.4 Collect the upper layer (Acetonitrile) in a 100ml erlenmeyer flask. Approximately 10ml should be collected.

11.1.5 Add another 10ml of acetonitrile into the 1000ml erlenmeyer flask containers sample and stir on high speed for 15 minutes. Allow the phases to separate for about 10 min. Collect the upper layer and combine with the first extract in the 100ml volumetric flask.

11.1.6 Prepare a salt water solution in a separate flask by dissolving 325g of NaCl in 1000ml of D.I. water. Add 84ml of the salt water solution to the extract, which was collected in a 125ml erlenmeyer flask. Place the 125ml erlenmeyer flask on the magnetic stirrer with a magnetic bar and stir on high speed for 15 min. Allow the separation of the layers. Collect the top layer (Acetonitrile), extract one more time with an additional 1ml of acetonitrile, adding this to the first extract and adjust the volume to 10ml using Class A graduated cylinder.

11.1.7 Before analysis dilute the sample 1:1 with Dilwater (with phenol if dinoseb is a suspected analyte) prior to analysis.

11.2 Soil and Sediment Samples

11.2.1 Sample homogenization: Air dry soil samples at room temperature for 24 hours, being careful not to expose the samples to direct sunlight. Visually inspect the sample to insure that no clumps exist. Weigh the sample and record the results in the extraction logbook. Continue to monitor the sample weight every two hours until constant weight is reached. The acceptance criteria is a 1% variation in weight. Record the initial and subsequent results. Homogenize the dried sample thoroughly and grind clumps with a spatula so that it can pass through a 30 mesh sieve. Rinse spatula with acetonitrile and dry after every sample. To prevent cross contamination of samples, sieve must be cleaned thoroughly and dried after every use.

11.2.2 Place 2.0g subsample of each soil sample in a 40ml glass vial. Add 9.0ml of acetonitrile and 1.0ml of 6ppm surrogate to each sample. Add 8.0ml of acetonitrile and 1ml of 8330 matrix spike, 1.0ml surrogate to each LCS and sample matrix spike.

11.2.3 Place samples in a cooled ultrasonic bath for 18 hours. After sonication, allow sample to settle for 30 minutes. Remove 5.0ml of supernatant, and combine with 5.0ml of calcium chloride solution before filtering through a 0.45um teflon filter. Discard the first 1.0ml of extract and collect the remainder for HPLC analysis. Allow samples to equilibrate for 15 minutes before analysis.

12.0 SAMPLE ANALYSIS

12.1 Sample analysis may begin when calibration is complete.

12.2 Mid-Point standards are run every ten samples in order to examine both the variation of retention time and to check the calibration of the instrument.

12.3 A dilution must be performed when the peak response exceeds the calibration range of the compounds.

12.4 Peak identification is based on the comparison of the retention times using both the primary and confirmatory columns. A retention time window is calculated by using the average retention time ± three times the standard deviation of 3 mid points during 72 hours of analyses. The average retention time is determined whenever column change or equipment maintenance is performed.

12.5 The following explosive compounds can also be determined by modified 8330 procedure

PETN. PETN can be identified and quantified by method 8330. Extraction procedure for PETN is the same as 8330 target compound list. Matrix and lab blank samples (LCS) are spiked at 0.4ml of 10ug/ml PETN for water and soil samples. Surrogate solution is spiked at [illegible] ml collected [illegible] for water and soil samples. Chromatographic conditions for the analysis of PETN includes

- Mobil phase: acetonitrile/water 50/50
- Flow rate: 1.2ml/min
- Wavelength: 254nm
- Injection volume: 100ul

Nitroglycerine. Nitroglycerine can be identified and quantified by method 8330. Extraction procedure for Nitroglycerine is the same as 8330 target compound list. Matrix and lab blank samples (LCS) are spiked at 1.0ml of 200ug/ml nitroglycerine for water and soil samples. The following chromatographic conditions are used for Nitroglycerine analysis:

- Mobil phase: 50/50 Methanol/water
- Flow rate: 1.0ml/min
- Wavelength: 254nm
- Injection volume: 100ul

Picric Acid. Picric acid can be identified and quantified by method 8330. Extraction procedure for picric acid is the same as 8330 target compound list. Matrix and LCS are spiked at 0.2ml of 100ug/ml for water and soil samples. The following chromatographic conditions are used for picric acid analysis:

- Mobil phase: Tetrabutylammonium buffer at 1.7g in 0.5 lit acetonitrile and 0.5 lit water solution
- Flow rate: 1.5ml/min
- Wavelength: 365
- Injection volume: 50ul

Diazodinitrophenol (DDNP). DDNP can be identified by a modified method 8330. Extraction procedure for DDNP is the same as 8330 method for the target explosive compound list. Matrix spikes and LCS are spiked at 0.4ml of 10ug/ml DDNP for water and soil matrices. The following chromatographic conditions are used for DDNP analysis:

- Mobile phase: Acetonitrile/H_2O, 50/50
- Flow rate: 1.2ml/min
- Wave length: 204nm
- Injection volume: 100ul
- Column: C_{18}

13.0 SAMPLE QUANTITATION

The concentration of all target compounds should be calculated using the following equations

13.1 Water Sample

Conc (ug/L) $\frac{\text{(Peak Area/Height of Sample)(Final Volume in ml)(Dilution)}}{\text{(Avg RF of Std)(Initial Volume in ml)}}$

13.2 Soil Sample

Conc (ug/Kg) $\frac{\text{(Peak Area/Height of Sample)(Final Volume in ml)(Dilution)}}{\text{(Avg RF of Std)(Initial Wt in gm)}}$

13.3 2,4-DNT and 2,6-DNT co-elute on the primary column and the confirmation column. The peak area of 2,4-DNT and 2,6-DNT in the LCS and MS/MSD samples is quantitated and reported as 2,4-DNT. A peak detected in the retention time window of 2,4-DNT and 2,6-DNT on both columns will be reported as an isomeric pair in samples.

13.4 Degradation products of tetryl appear as a shoulder on the 2,4,6-TNT peak. 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.

14.0 QUALITY CONTROL

14.1 A method blank is extracted and analyzed with every batch of 20 samples or less. The level of target analyte contaminants in the blank must be less than the reported detection limits.

14.1.1 If the contamination in the blank is not within the acceptable level, all samples associated with contaminated blank must be re-extracted and re-analyzed.

14.1.2 Blank must be spiked with surrogate specified in section 11.1.1. If the surrogate recovery in the method blank does not meet the in-house established acceptance criteria, first re-analyze the method blank. If the surrogate recovery does not meet the acceptance criteria after the re-analysis, the method blank and the sample associated with the blank must be re-extracted and re-analyzed.

14.2 Sample analysis

14.2.1 Sample must be extracted and analyzed with the holding times specified in section 7.0.

14.2.2 The samples must have associated method blank meeting the blank acceptance criteria.

14.2.3 Samples must be spiked with surrogate specified in section 11.1.1. If the surrogate recovery does not meet the in-house established acceptance criteria, first check calculation, sample preparation logs, and the instrument condition. If calculation was uncorrect, correct the calculation and verify that the surrogate compound recovery meets the acceptance criteria. If the instrument malfunctioned, correct the instrument problem and re-analyze the sample extract.

14.2.4 If the above action does not correct the problem, re-extract and re-analyze the sample.

14.2.5 If the surrogate compound recovery meets the acceptance criteria in the re-extraction, submit the data from the re-extraction.

14.2.6 If the surrogate compound recovery fails to meet the acceptance criteria in the re-extracted samples, then the problem may be due to matrix effect. To determine if there was matrix effect, review the surrogate recoveries of blank, LCS & MS/MSD analyzed and extracted in the same batch.

14.3 Laboratory Control Sample

Laboratory Control Sample (LCS) is extracted and analyzed for every batch of 20 samples or less. The recovery limits are determined by taking three standard deviations of 20 consecutively analyzed LCS's. Recovery limits are updated periodically. Data points used in the data set must not be selectively included or excluded.

The LCS is analyzed to assess general method performance. The LCS is spiked with all target analyses before it is carried through the sample preparation. For soil samples, a purified solid matrix (e.g., ottawa sand, sodium sulfate, or other purified solid) would typically be used. For aqueous analyses, use analyte-free reagent water. The concentration used to spike the LCS is the 3rd level of the initial calibration mix A and mix B (see tables II and III).

14.3.1 If any analytes fail to meet the laboratory established QC criteria, first re-analyze the LCS. Two LCS compounds can be outside the laboratory established QC limit. No compound can grossly exceed the acceptance limit in the LCS (50% - 150%). If the LCS does not meet the above criteria, then the LCS method blank and all associated samples of the batch would be re-prepared and re-analyzed.

14.4 Matrix spike and duplicate analyses are performed per batch of 20 samples or less.

The MS/MSD is evaluated by comparing the precision of target analytes to the recovery windows established. MS/MSD data evaluation is more complex than method blank or LCS data since MS/MSD measure matrix effect in addition to sample preparation and analysis error. MS/MSD that fail to meet the acceptance criteria would indicate that a potential matrix effect is present. The laboratory must assess the batch to determine whether the spike results are attributable to matrix affect, or the result of other problem in the analytical process. If all the QC batch elements which are not affected by the sample matrix are in control (e.g., method blank, LCS), and if there is no evidence that the spiking was not properly performed, the poor spike recovery may be attributed to matrix effect. If the LCS compounds that are not affected by the sample matrix are in control, and if the same compounds in the MS/MSD are outside control limits, then matrix spiked sample(s) must be re-processed through the analytical sequence. RPD for the MS/MSD should [illegible]%.

14.5 Confirmation for all target compounds detected on the C18 column is performed on a CN column. CN column analysis is for qualitative purposes and depends on compound concentration detected on C18 column. CN column is generally less sensitive in comparison with C18 column. Analytes are identified when peaks are observed in the retention time window of the analyte on both columns. Confirmation of peak on the CN column is based on comparison of the retention time with corresponding peak of the standard analyzed before the sample. On the CN, for a peak to be confirmed, it must fall within the established retention time window of the standard obsolete retention time. When identification has been confirmed on the confirmation column, the analyst should evaluate the agreement of the quantitated results on both columns. Retention time windows is established by analyzing the mid-level standard in over the period of 72 hours. The window for that day will be plus or minus three times the standard deviation.

14.6 Surrogate recoveries are quantified for all blanks, samples, matrix spikes and lab control spikes. Surrogate recoveries should be established and monitored by plotting control charts. Recoveries of surrogate for the blank and samples should be within the specified ranges. If the recoveries of surrogate are outside the QC limits re-analyze the extract. Re-extraction of the sample should also be considered if re-injection of the sample produces similar results. The judgement of the experienced analyst is heavily relied upon when re-extraction and/or re-injection deem necessary.

15.0 SAFETY

15.1 Standard precautionary measures used for handling other organic compounds like safety glasses, laboratory coats, gloves should be sufficient for the safe handling of the analytes handled by this method. The only extra caution should be taken is when handling the analytical standard neat material.

15.2 Visual observation of soil sample is important when the sample is taken from a site expected to contain explosives lump of material that have a chemical appearance should be suspect and not ground. Explosives are generally a very finely ground grayish-white material.

16.0 POLLUTION PREVENTION

16.1 GPL Laboratory operates in a safe manner to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. For more detail on pollution prevention, refer to GPL SOP [illegible]

17.0 WASTE MANAGEMENT

17.1 Several wastes that GPL generates can be handled in a fairly routine manner. The process of describing the method for waste disposal of chemicals including standards and reagent solutions, and [illegible] waste, and [illegible] described in Standard Operating Procedures D.1 and D.2.

18.0 DEFINITIONS

18.1 For definitions of terms used in this document, refer to GPL Laboratory SOP G.14

SOP No: H.21

Title: Acid Digestion of Soil, Sludge, Sediment, and Other Solid Waste Samples for ICP by SW846 Method 3050B.

Scope: The method detailed in this procedure is performed to prepare soil, sediment, sludge and other solid samples for quantitation of certain metallic analytes using Inductively Coupled Plasma (ICP), in accordance with SW846 Method 3050B.

1.0 PURPOSE

1.1 The method detailed in this procedure is used to prepare solid waste samples for analysis using an Inductively Coupled Plasma (ICP) spectrophotometer. The sample holding time before extraction is 180 days. Samples must be stored in refrigerator at 4°C until time of preparation. The elements to be analyzed using this procedure are

ICP Elements
Al
Ba
Be
Cd
Ca
Cr
Co, Ag
Cu, As
Fe, K
Mg, Na
Mn, Pb
Ni, Sb
V, Se
Zn, Tl

This method is also applicable to other metals (B, Mo, Sr, Sn, Ti).

2.0 REFERENCES

- SW846 method 3050B revision 2, December 1996.

3.0 EQUIPMENT AND SUPPLIES

- 150ml beakers/or hot block vessels
- Analytical balance accurate to 0.001 grams
- 100ml volumetric flasks
- Hot plate, or hot block capable of maintaining temp. of 90-95 degrees C.
- Whatman No. 41 filter paper
- 250ml sample bottle (plastic)
- Watch glass, ribbed
- Plastic disposable funnels
- Thermometer, calibrated, NIST traceable
- Fume hood
- Pipetters (calibrated)
- Bottle top dispensers used to add all reagents
- Teflon coated spatula

4.0 REAGENTS

- Concentrated Nitric Acid - trace metals grade
- 1:1 Nitric Acid trace metals grade
- Concentrated Hydrochloric Acid - trace metals grade
- Metals Standards - commercially prepared NIST traceable metals standards with documented concentrations, including impurities and expiration dates (Vendor: High Purity Standards, Charleston, SC).
- 30% Hydrogen Peroxide
- Grade and quality of water required is ASTM Type II water (ASTM D1193): Water must be monitored for changes in conductivity by laboratory staff and is currently provided by a laboratory pure water system.

5.0 PROCEDURE

5.1 Sample Digestion Procedure

5.1.1 Mix the sample thoroughly to achieve homogeneity using a spatula. For each digestion procedure, weigh (to the nearest .01g) 1-2g portion of sample and transfer to a beaker/vessel.

Note: A separate sample shall be dried for percent solids determination. See SOP "Percent Solids Determination Procedure".

5.1.2 Label two beakers/vessels, one as a sample and the second as a duplicate

5.1.3 Label one beaker/vessel as matrix spike. To matrix spike beaker/vessel add 0.2mL each of spiking solution (ICP SPK1,2,3) after addition of 10mls of 1.1 nitric acid

5.1.4 Take one beaker/vessel and label as prep blank (BLK).

5.1.5 Take beaker/vessel and label as BKS. To BKS beaker/vessel add 0.2mL each of spiking solution (ICP SPK1,2,3) after addition of 10mls of 1:1 nitric acid.

5.1.6 To all beakers/vessels, add 10ml of 1:1 nitric acid (HNO_3) [illegible] and cover with a watch glass. Heat the sample on a hot plate in the fume hood to 95°C (± 5°C) and reflux for 30 minutes without boiling. Allow the sample to cool, add 5ml of concentrated (HNO_3) [illegible] the watch glass, and reflux for 30 minutes. Repeat the concentrated (HNO_3) addition until no brown fumes are given off by the sample. [illegible] a covering of solution over the bottom of the beaker/vessel [illegible] the temperature achieved during the digestion with a beaker containing 50ml ASTM type II water. Record temperature in digestion log. Using a ribbed watch glass either allow the solution to evaporate to approximately [illegible] without boiling OR heat at 95°C ± 5°C without boiling for [illegible]

5.1.7 After the sample has cooled, add 2ml of 30% hydrogen peroxide (H_2O_2) and cover with watch glass. Return the beaker/vessel to the hot plate/hot block 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, then cool the beaker.

5.1.8 Repeat step 5.1.7 until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10ml 30% H_2O_2).

5.1.9 Add 3ml of 30% hydrogen peroxide (H_2O_2), heat the acid-peroxide digestate to 95°C ± 5°C until the volume has been reduced to approximately 5mL without boiling OR for two hours at 95°C ± 5°C without boiling

5.1.10 Add 10ml of concentrated HCl, return the covered beaker to the hot plate, and heat for an additional 15 minutes at 95°C (± 5°). After cooling, filter through Whatman No. 41 filter paper (or equivalent) using disposable funnel and dilute in a 100ml volumetric flask with Type II water. The diluted sample has an approximate acid concentration of

10% (v/v) HCl and 5% (v/v) HNO_3. Transfer the sample diluted sample to a 125mL plastic sample bottle labeled with the work order, fraction, and date of digestion. Date of digestion may by put on the box of digestates instead of on each bottle. The sample is now ready for analysis.

6.0 METHOD PERFORMANCE

6.1 Per digestion method MDL limits are obtained by digestion of seven spiked replicates in the same way as samples and analyze them. MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. Precision and accuracy studies are performed once a year at a minimum.

7.0 METHOD DETECTION LIMIT

7.1 Method detection limits for this method are listed in the GPL Laboratory Method Detection Limit and Reporting Limit official book.

8.0 DEFINITIONS

8.1 For definitions of terms used in this document, refer to GPL Laboratory SOP G.14.

9.0 QUALITY CONTROL

9.1 Troubleshooting and corrective action.

9.1.1 The ICP operator should report to his/her supervisor and lab manager any recoveries outside warning limits for BKS samples for analytes being determined. Sample recoveries for any element which are outside of the control established limits for the laboratory control sample, are deemed unacceptable. The digestion batch must be re-digested for those analytes. Document the incident on a re-digestion form and submit to supervisor.

10.0 SAFETY

10.1 Safety equipment required

- Fume hood - minimum flow of 100 linear feet/minute
- Safety glasses
- Safety gloves (unpowdered)
- Lab apron
- Face shield, if necessary

10.2 Potential hazards

The most hazardous chemical acids that laboratory personnel are likely to encounter are strong acids such as Hydrochloric Acid and Nitric Acid (HNO_3).

10.3 Special handling requirements

Analysts should always read the label on the bottle. Chemicals require handling with care to include wearing adequate garments for skin protection. Also, acids should be handled only under a ventilated hood.

11.0 POLLUTION PREVENTION

11.1 GPL Laboratory operates in a safe manner to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. For more details on pollution prevention, refer to GPL SOP D.5.

12.0 DISPOSAL REQUIREMENTS

12.1 Acid wastes should be placed into the acid waste bottle which is located in the metals digestion lab. Any remaining samples should be returned to sample control. More details concerning disposal characteristics and procedures can be located in the SOP "Laboratory Waste Handling and Storage Procedure".

13.0 REPORTING REQUIREMENTS

13.1 Documentation to include Work Orders and Metals Preparation and Sample Description log must be submitted to the Metals Supervisor with the Digestion Technician's initials and the preparation date documented on each form for each batch.

Sample Description must be filled out and should contain the following information for aqueous digestates. The fields for color and clarity, before and after digestion, must be completed. The following descriptive terms are recommended:

Color - red, blue, yellow, green, orange, violet, white, colorless, brown, gray, black

Clarity - clear, cloudy, opaque

Texture - coarse, medium, fine

Note any significant changes that occur during sample preparation (i.e., emulsion formation) in the Comments section. Enter any sample-specific comments concerning the analyte results in the comments section. If ICP analysis is required, use color of ICP digests for sample description.

Metals Preparation and Sample Description Log Forms (Figure 1) must be documented completely by the Digestion Technician during digestion and include the date of digestion, work order number, digestion technician signature, supervisor initials, identification of method used, Lab Sample ID, sample matrix (soil/water), amount of sample used in digestion and final volume of sample, identification of the matrix spiking solution used, the amount used, and identifications of any reagents used during the digestion.

13.2 QC records are maintained in the form of control charts to document percent recovery of analytes See SOP "Quality Control Charts" for more information.

Figure 1

Metals Digestion Logform

Date: Prep: 200.7 / 3005A / 3C20A / 3050B / 3010A / ILC03.1 / ILM04.1 / ILM05.1 Batch No: 83-

Analyst: Comments:

Reviewed by: Date Spike Witness: Prep. Seq:

	GPL Work Order No.	Sample	Frac	SIZE mL (g)	Final Vol. (mL)	Matrix S, W Other	Color Before R, Bl, Y, G, O, V, Br, Colorless	Color After R, Bl, Y, G, O, V, Br, Grey, Bk.	Clarity Before or Soil Texture	Clarity After Clear, Cloudy, Opaque	Soil Artifacts or Water pH
1											
2											
3											
4											
5											
6											
7											
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21											
22											
23											
24											

LCS ID / Amt. Added (ml, g):	HNO3(1+1) ID:
Spiking ID / Amt Added (ml)	HNO3(conc) ID:
	HCl(conc) ID:
Temperature, C:	HCl(1+1) ID:
	Peroxide ID:

SOP No: H.8

Title: Acid Digestion of Aqueous Samples, EP and TCLP Extracts and Waters that Contain Suspended Solids for Flame/ICP Analyses and Furnace Analysis of Antimony in Accordance with SW846 Method 3010A

Scope: The method detailed in this procedure is performed to prepare aqueous samples and extracts for quantitation of certain metallic analytes using Inductively Coupled Plasma (ICP) or Flame Atomic Absorption (FLAA) or Graphite Furnace Atomic Absorption for antimony (GFAA) spectroscopy in accordance with SW846 method 3010A.

1.0 PURPOSE

1.1 The method detailed in this procedure is used to prepare aqueous samples and extracts for analysis using an Inductively Coupled Plasma (ICP) spectrophotometer or Flame Atomic Absorption (FLAA) spectrophotometer or Graphite Furnace Atomic Absorption for antimony (GFAA). The sample holding time before digestion is 180 days. The elements to be analyzed using this procedure are:

Ag, Al, As, Ba, Be, Cd, Ca, Cr, Co, Cu, K, Fe, Pb, Na, Ni, Mg, Mn, Se, Sb, Tl, V, Zn, B, Sr, Ti, Sn, Mo.

2.0 REFERENCES

- SW846 method 3010A revision 1

3.0 EQUIPMENT AND SUPPLIES

- 150mL glass beakers
- 100ml volumetric flasks
- Hot plate
- Whatman No. 41 filter paper
- 125ml sample bottle (plastic)
- Watch glass (non-ribbed)
- Watch glass (ribbed)
- Plastic disposable funnels

- Thermometer, calibrated, NIST traceable
- Fume hood
- Eppendorf and Oxford pipettors (calibrated)
- 100ml graduated cylinders

4.0 REAGENTS

- Concentrated Nitric Acid - trace metals grade
- Concentrated Hydrochloric Acid - trace metals grade
- 1:1 Hydrochloric Acid - to 500ml ASTM type II water (see below) add 500ml of Concentrated Hydrochloric Acid
- Metals Standards - (ICP spk 1,2,3) commercially prepared NBS traceable metals standards with documented concentrations, including impurities and expiration dates. (Vendor: High Purity Standards, Charleston, SC).
- Diluent for ICP & FLAA standards - Flame Water. Flame water is prepared by adding 200ml concentrated nitric acid and 1000ml concentrated hydrochloric acid to 20 liters deionized water.
- Grade and quality of water required is ASTM Type II water (ASTM D1193): Water must be monitored for changes in conductivity by laboratory staff and is currently produced by the laboratory pure water system.

5.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

5.1 All sample containers must be prewashed with detergents, acid, and water. Plastic and glass pint containers are both suitable.

5.2 Non-aqueous samples shall be refrigerated upon receipt and analyzed as soon as possible.

5.3 For detailed information about preservation, storage and handling of samples, refer to GPL SOP F.2.

6.0 PROCEDURE (see Figure 1 for flow chart)

6.1 Sample Digestion Procedure

6.1.1 Mix the sample thoroughly to achieve homogeneity. Transfer 100ml of sample using a graduated cylinder to a beaker. Transfer 100ml of sample each for duplicate and matrix spike analysis and label as duplicate and matrix spike. For extracts of TCLP or highly contaminated wastes, reduce size to 10.0ml.

6.1.2 If aqueous samples are to be analyzed, to the matrix spike beaker, add 0.2ml of matrix spike solution (ICP spk 1,2,3).

6.1.3 If sample extracts are to be analyzed, to the matrix spike beaker, add 0.2mL of matrix spike solution (ICP spk 1,2,3).

6.1.4 Label one empty beaker "BKS" for the laboratory control sample. Add 100ml ASTM type II water to the beaker. Add 0.2mL of matrix spike solution (ICP spk 1,2,3).

6.1.5 Label one empty beaker "BLK" for the preparation blank. Add 100ml ASTM type II water.

6.1.6 To all beakers, add 3mls of concentrated nitric acid (HNO_3) and cover the samples with ribbed watch glasses.

6.1.7 Heat on a hot plate in the fume hood and evaporate until volume is approximately 5mls. Do not boil or allow beaker to go dry. Remove beaker from hot plate and allow to cool.

6.1.8 After cooling, add 3mls of concentrated nitric acid and cover samples with a non-ribbed watch glass. Return to hot plate and increase temperature to reflux gently.

6.1.9 Continue to heat, adding additional acid if necessary, until the digestate is light in color. Uncover the samples and evaporate to approximately 3mls.

6.1.10 Remove samples from hot plate and allow to cool. Add 10ml of 1:1 hydrochloric acid.

6.1.11 Cover the beakers and reflux for 15 minutes.

6.1.12 Wash down beaker walls and filter sample, if necessary, through Whatman No. 41 filter paper (or equivalent) using disposable funnel. Dilute to 100ml in volumetric flask with Type II water.

NOTE. In place of filtering, the sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. Filter or centrifuge the sample only when sample contains insoluble materials that may clog the nebulizer. The diluted digestate solution contains approximately 5% (v/v) HCL and 3% HNO3. Transfer to 125ml plastic sample bottle and label with GP work order, fraction, WFL (for water matrix, flame/ICP digestion) and date of digestion. Date of digestion may be put on the box of digestates instead of on each bottle. For analysis, withdraw aliquots of approximate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.0 QUALITY CONTROL

7.1 Troubleshooting and corrective action.

The furnace, ICP and flame AA operators should report to his/her supervisor and lab manager any recoveries outside warning limits for LCS samples for analytes being determined or preparation blanks are above control limits. Sample recoveries for any element which are outside of the control established limits for the laboratory control sample or contaminated preparation blanks are deemed unacceptable. The digestion batch must be re-digested for these analytes. Document the incident on a re-digestion form and submit to supervisor.

8.0 SAFETY

8.1 Safety equipment required

- Fume hood - minimum flow of 100 linear feet/minute
- Safety glasses
- Safety gloves (unpowdered)
- Lab apron
- Face shield, if necessary

8.2 Potential hazards

The most hazardous chemical acids that laboratory personnel are likely to encounter are concentrated solutions as Hydrochloric Acid and Nitric Acid (HNO_3).

8.3 Special handling requirements

Analysts should always read the label on the bottle. Chemicals require handling with care to include wearing adequate garments for skin protection. Also, acid use should be performed under a ventilated hood.

9.0 DISPOSAL REQUIREMENTS

9.1 Acid wastes should be placed into the acid waste bottle which is located in the metals digestion lab. Any remaining samples should be returned to sample control. More details concerning disposal characteristics and procedures can be located in the SOP D 1 "Laboratory Waste Handling and Storage Procedure".

10.0 POLLUTION PREVENTION

10.1 GPL Laboratory operates in a safe manner to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. For more detail on pollution prevention, refer to GPL SOP D.5.

11.0 DEFINITIONS

11.1 For definitions of terms used in this document, refer to GPL Laboratory SOP G.14.

12.0 REPORTING REQUIREMENTS

12.1 Documentation to include Work Orders and Work Sheets (see SOP "Sample Logging and Record Keeping"), Metal Digestion Log Forms must be submitted to the Metals Supervisor with the Digestion Technician's initials and the preparation date documented on each form for each case.

Sample Description Information must be filled out and shows [illegible] following information for aqueous digestates. The fields for color and [illegible], before and after digestion, must be completed. The following descriptive terms are recommended:

Color - red, blue, yellow, green, orange, [illegible], white, [illegible], gray, black

Clarity - clear, cloudy, opaque

Note any significant changes in color during sample preparation (i.e., emulsion formation) in the comments section. Enter any sample-specific comments concerning the analytical results in the comments section.

Metal Digestion Log Forms (Figure 2) must be documented completely by the Digestion Technician during digestion include the date of digestion, work order number, digestion technician signature, supervisor approval, identification of methods used, GPL Laboratory ID, sample matrix (soil/water), amount of sample used in digestion and final volume of sample, identification of the matrix spiking solution used and the amount used.

12.2 QC records are maintained in the form of control charts to document percent recovery of analytes from EPA ICV and independent laboratory control samples subjected to the digestion procedure.

Figure 1

FLOW CHART

ACID DIGESTION OF AQUEOUS SAMPLES OR EXTRACTS
FOR ANALYSIS ICP/FLAME AA OR SB BY GFAA

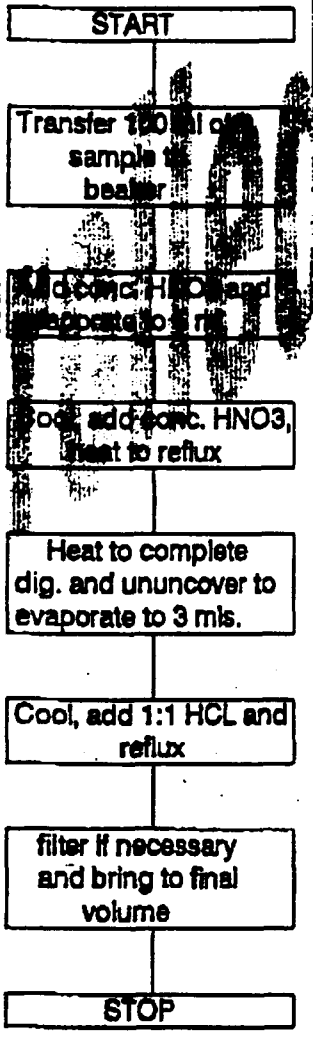

Figure 2

Metal Digestion Log Form

Date: Prep: 200.7 / 3005A / 3020A / 3050B / 3010A / ILC03.1 / ILM04.1 / ILM05.1 Batch No: 83-

Analyst: Comments.

Reviewed by: Date Spike Witness: Prep. Seq:

	GPL Work Order No.	Sample	Frac	SIZE mL (g)	Final Vol. (mL)	Matrix S, W Other	Color Before	Color After	Clarity Before	Clarity After	Soil Artifacts
							R, Bl, Y, G, O, V, W, Colorless, Br, Grey, Bl		Soil		
1											
2											
3											
4											
5											
6											
7											
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22											
23											
24											

LCS ID / Amt. Added (ml , g) :	HNO3(1+1) ID:
Spiking ID / Amt Added (ml):	HNO3(conc) ID:
	HCl(conc) ID:
Temperature, C:	HCl(1+1) ID:
	Peroxide ID:

SOP No: H.10

Title: Trace ICP Quantitation of HSL Metals plus Boron, Molybdenum, Silicon, Strontium, Titanium, and Tin According to Method 6010B

Scope: The method detailed in this procedure is for the analysis of water, TCLP and EP extracts, soils, sludges, sediments and other solid wastes digestates for Hazardous Substance List (HSL) Metals by Inductively Coupled Plasma (ICP) spectroscopy in accordance with USEPA method 6010B. The use of ionization buffers, internal standards, and special background correction techniques is specified

1.0 INTERFERENCES

1.1 There are many categories of interferences: unresolved overlap of molecular band spectra, stray light, overlap from nearby spectral lines, and background emission from continuous or recombination phenomena.

2.0 PURPOSE

2.1 The purpose of this procedure is to describe the simultaneous analysis of metals on the USEPA Hazardous Substances List (Antimony, Arsenic, Lead, Selenium, Silver, Thallium, Sodium, Potassium, Aluminum, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Magnesium, Manganese, Nickel, Vanadium, and Zinc) plus Boron, Molybdenum, Strontium, Titanium, and Tin at trace levels using a Thermo-Jarrell-Ash 61E Purged Trace Inductively Coupled Plasma Spectrometer and autosampler. All samples are digested in accordance with SOP H 4 or H 5 prior to analysis. Filtered samples for dissolved metals analysis can be analyzed after either digestion or matrix matching. The digestate holding time is 180 days

3.0 REFERENCES

- TJA ICAP 61E Operator's Manual (p/n 134542-00).
- SW846 method 6010B revision 1

4.0 EQUIPMENT AND SUPPLIES

- 100mL volumetric flasks
- 200mL volumetric flasks
- 500mL volumetric flasks
- 1000mL volumetric flasks
- 100mL plastic storage bottles
- 250mL plastic storage bottles
- 500mL plastic storage bottles
- 1000mL plastic storage bottles
- 20.0L Nalgene carboy
- 10.0L Nalgene carboy
- 15mL disposable autosampler tubes
- 28mL disposable autosampler tubes
- Centrifuge tube holder
- Pipetters and Pipette Tips
- 5, 10, 20mL class A volumetric pipets
- Pump windings and tee fittings
- Argon gas (cryogenic liquid source)
- Nitrogen gas (cryogenic liquid source) used for purging of spectrometer

4.1 Instrumentation

4.1.1 TJA 61E Purge Trace ICP with meinhard nebulizer, cyclonic spray chamber, horizontal torch, and AS-192 autosampler.

4.1.2 Simultaneous background correction technique is used for the analysis of lead and selenium to achieve lower instrumental detection limits comparable to graphite furnace.

4.1.3 An argon humidifier is used for extracts and samples containing high salts. A high-solids "Bergener" nebulizer can be used for the analysis soil digestates.

4.1.4 Yttrium Internal standard - Lithium ionization buffer is added on-line using a mixing tee and coil with a ratio of 1:4 (one part standard: four parts samples, resulting in a dilution factor of 5 for the internal standard, approximated 10ppm is the final "mixed-in" concentration.

5.0 REAGENTS

- A deionized water ASTM type II or equivalent
- Concentrated hydrochloric acid, trace metals grade
- Concentrated nitric acid, trace metals grade
- Flame Water - 5% hydrochloric acid, 1% nitric acid

Preparation of Reagent Flame Water

Fill a 20L Nalgene carboy half full with type II water. Add 200ml concentrated nitric acid and 1000ml concentrated hydrochloric acid underneath a hood to contain noxious gases. Dilute to twenty liters with type II water and mix thoroughly.

2% nitric acid

5ppm Arsenic Profile check solution

Preparation of Arsenic Solution:

Pipette 2.5mL of 1000ppm Arsenic stock solution into a 500mL volumetric flask. Dilute to volume with matrix matched water. Transfer to a bottle labeled 5ppm ml. Record the date of preparation, expiration date and preparer initials on the bottle label. Prepare Arsenic Profile solution every three months or when depleted, whichever is more frequent.

50ppm Y-1500ppm lithium internal standard solution buffer

Preparation of 50ppm Y-1500ppm Lithium internal standard solution buffer

Pipet 100mls of GP mix L into 1000ml volumetric flask. Dilute to volume with flame water.

All stock and prepared standards are logged into a software program (solutions manager). All stock and prepared standards are assigned a solutions manager reference number. The reference number expiration date, prep date and chemist initials are written on a label and placed on all prepared solutions. The expiration date chosen by solutions manager for prepared standards is three months for the prepared date.

6.0 GENERAL PRECAUTIONS

6.1 AVOID CONTAMINATION of STOCK STANDARDS. Always pour a small volume of standard stock solution into a new microbeaker before pipetting an aliquot. NEVER insert a pipette directly into the bottle. This precautionary measure also applies to quality control standards stock solutions (ICVA, IC1, etc.)

6.2 Check pipetters daily for leaks and proper calibration. Record in the pipette log book.

6.3 Empty Drain vessel at the end of each day. Transport waste to the waste disposal area for appropriate treatment prior to shipment. Fill vessel up to 6 inches using tap water prior to replacing vessel beneath instrument.

6.4 Clean up and neutralize all spills immediately to avoid corrosion damage to the instrument.

6.5 Purge the optics with nitrogen at all times. Leave the RF power unit on at all times. Never attempt to perform repairs to the High voltage systems. Leave the instrument PM tubes and heater on at all times.

7.0 PROCEDURE

7.1 Preparation of Calibration Standards

7.1.1 To prepare calibration Standard 1 in flame water, pipette 25mL of source solution Sp Mx Std. 12 into a 500mL flask, which has been half filled with flame water. Dilute the flask to volume with flame water. Mix the solution thoroughly, and transfer it to a plastic bottle.

True value of Standard 1

Element	Certified Std Conc (ug/ml) Added	Volume (ml)	Calibration Std. Conc. (ug/L)
Aluminum	1000	25	50000
Antimony	20	25	1000
Arsenic	20	25	1000
Barium	10	25	500
Beryllium	1.000	25	50
Boron	10	25	500
Cadmium	10	25	500
Chromium	10	25	500
Cobalt	10	25	500
Copper	10	25	500
Iron	1000	25	50000
Lead	10	25	500
Manganese	10	25	500
Molybdenum	10	25	500
Nickel	10	25	500
Selenium	20	25	1000
Silicon	10	25	500
Silver	1.000	25	50
Strontium	10	25	500
Thallium	20	25	1000
Tin	10	25	500
Titanium	10	25	500
Vanadium	10	25	500
Zinc	10	25	500

7.1.2 To prepare calibration Standard 2 in flame water, pipette 50mL of source solution Sp Mx Std. 12 into a 500mL flask, which has been half filled with flame water. Dilute the flask to volume with flame water. Mix the solution thoroughly, and transfer it to a plastic bottle.

True value of Standard 2

Element	Certified Std. Conc.(ug/ml) Added	Volume (ml)	Calibration Std. Conc. (ug/L)
Aluminum	1000	50	100000
Antimony	20	50	2000
Arsenic	20	50	2000
Barium	10	50	1000
Beryllium	1 000	50	100
Boron	10	50	1000
Cadmium	10	50	1000
Chromium	10	50	[illegible]
Cobalt	10	50	[illegible]
Copper	10	50	[illegible]
Iron	1000	50	[illegible]
Lead	10	50	[illegible]
Manganese	10	50	[illegible]
Molybdenum	10	50	[illegible]
Nickel	10	50	[illegible]
Selenium	20	50	[illegible]
Silicon	10	50	1000
Silver	1.000	50	100
Strontium	10	50	1000
Thallium	[illegible]	50	2000
Tin	[illegible]	50	1000
Titanium	[illegible]	50	1000
Vanadium	10	50	1000
Zinc	10	50	1000

To prepare calibration Standard 3 in flame water, add 5ml each of the Mg, Ca, Na stock (10,000ppm) and 1.250ml of K stock standard (10,000ppm) standard from High Purity standard with a Class A volumetric pipets to a 250mL volumetric flask which has been half filled with flame water. Dilute the flask to volume with flame water, mix the solution thoroughly, and transfer to a plastic bottle.

Standard 3	Starting CONC	Volume Added	Final CONC.
Sodium	10,000ug/ml	5.0ml	200000ug/L
Potassium	10,000ug/ml	1.25ml	50000ug/L
Magnesium	10,000ug/ml	5.0ml	200000ug/L
Calcium	10,000ug/ml	5.0ml	200000ug/L

NOTE 1. These formulations are subject to change without an update of SOP to suit various client requirements

NOTE 2. A multipoint calibration is performed daily for those elements in standards 1 and 2. Standard 3 is used to perform a five point calibration that is re-sloped daily.

7.1.4 Document the standard in solutions manager program. Label the standard solution bottle. The label should include the preparers initials, the date of preparation, the expiration date, and the page number on which the standard has been recorded in the log book. The expiration date of standard solutions is three months from the date of preparation or whenever one of the certified standards expires, whichever is first.

7.2 QC Preparation

7.2.1 Preparation of Low level linearity check Solution.(PQL)

Pipette appropriate volume of single element STP's into 1000mL volumetric flask. Fill to volume with flame water.

Note: Additional elements can be added, if necessary, according to client needs

Document the solution in the Solutions Manager Software Program. Label the bottle as ICP Stock and record the preparation date, the expiration date, the preparers initials, and the ID number.

7.2.2 The CCV is made from the stock solutions used in making the calibration standards. The CCV concentrations are at half the concentrations of the highest standards used in calibration.

7.2.3 Initial Calibration Verification (ICV)

Fill a 1L volumetric flask halfway with flame water and add ten mLs of ICV, part 1 and part 2 certified stock solution. Dilute the flask to volume with flame water. Mix the solution thoroughly and transfer to a plastic bottle labeled ICV.

7.2.4 Interference Check Standard A (ICSA):

Fill a 500mL volumetric flask halfway with flame water and add 50mL of ICSA certified multi-element stock solution. Dilute the flask to volume with flame water. Mix the solution thoroughly and transfer to a plastic bottle labeled ICSA.

7.2.5 Interference Check Standard AB (ICSAB):

Fill a 500mL volumetric flask halfway with flame water and add 50mL of ICSA certified stock solution, and 0.500mL of ANALCS-R-2 certified stock solution and 5.0mL of ANALCS-R. Dilute the flask to volume with flame water. Mix the solution thoroughly and transfer to a plastic bottle labeled ICSAB.

7.3 Preparation of 1:5 Serial Dilution (L)

Obtain the sample digestates for the case or SDG to be analyzed. Take the original sample digestate that corresponds to the sample designated for duplicate and matrix spike digestions for each SDG and matrix and prepare its serial dilution as follows:

Transfer 2mls of sample into 8mls flame water. Mix thoroughly.

7.4 Preparation of Post Digestion Spike

Obtain the sample digestates for the batch or SDG analyzed. Take the original sample digestate that corresponds to the sample designated for duplicate and matrix spike digestions for each batch and prepare the post spike as follows:

Transfer 10ml of sample into a sample tube. Remove 0.1mls of sample, then spike with 0.1ml of post spike solution. Mix thoroughly.

Note: If the matrix spike recovery is outside criteria, the sample may require spiking at alternate concentrations.

7.5 Tuning and Calibration of the ICP

7.5.1 Conduct a pre-startup inspection.

7.5.1.1 Argon and Nitrogen gas supply and drain vessel

Make sure there is an adequate supply of Argon. Check the float gauge in the liquid argon dewar which is located in the cylinder storage room. The argon line pressure regulator should be set at 80psi and the nitrogen line pressure should be set at 50psi.

Check the drain vessel beneath the ICP and empty it if full.

7.5.1.2 Torch box

Make sure all connections are secure and air tight, including the drain hose, nebulizer cap, argon lines.

7.5.1.3 Peristaltic pump

Install new flexible pump tubing every other day (the windings have three stops which allow for an extra day of use) or if the old one shows signs of flattening or stretching, and connect to the nebulizer with capillary tubing

7.5.2 Daily Start Up

7.5.2.1 Reset computer and instrument. Load the operating software called Thermospec by using the windows icon under Thermospec window or by typing "STNRUN" at the C: drive prompt in DOS.

7.5.2.2 Ignite plasma. Engage pump tubings. Under the menu heading SET UP, select CONTROL PANEL; then press F1 for Start Up followed by F9 for continue to begin the start up sequence which takes about 90 seconds.

7.5.2.3 Warm-up. Once the torch has been successfully lit, exit the start up submenu and go to the analysis menu. At the method prompt, enter "6010" and the peristaltic pump should begin pumping. Check the settings adjusted to following:

Torch gas HIGH
Auxiliary gas LOW
Nebulizer gas 0.5 [illegible] L/min
Approximate RF Power (W) 1250
Pump rate (RPM) 110

Fill the rinse water reservoir with the same matrix as the samples and set rinse time for 60 seconds. Fill the internal standard - lot[illegible] buffer reservoir.

7.5.3 Profile and prepare for sample analysis.

7.5.3.1 Place a 28ml autosampler cup filled with 5ppm As onto the last position (#19) on the "L" rack of the autosampler. Under the analysis submenu, press F6 to move autosampler and begin profile sequence. Once the autosampler has moved it will wait 35 seconds to allow for adequate uptake and equilibration of the test solution.

7.5.3.2 Start the profile sequence. Press F3 and then F1 to start the profile. The procedure takes approximately 63 seconds and returns a peak profile of the Arsenic line at 189.042 x 2nm (second order line).

7.5.3.3 Record the peak position and intensity in the daily maintenance logbook. The peak position should be within 0.3 units of the 0 position and the intensity should be around 6000 "counts". Print out the profile report and include it with the raw data to demonstrate that the spectrometer was correctly profiled. A drift greater than the specified tolerance could indicate a drastic barometric or thermal change since the last profile and warrants further investigation. (see trouble shooting.)

7.5.3.4 The calibration curve must consist of a blank and standards (refer to section 7.1.1). Use the average of two exposures for both standards and samples.

7.5.4 Prepare autosampler sequence.

Under Operation menu, select "Autosampler Setup". Load the default table name "trace" and enter the samples to be run under set 2. (maximum 192). Enter a CCV and CCB every 10 samples. Once finished, print out the table assignments by pressing F2.

7.5.5 Load autosampler with standards and samples according to the table printouts. A typical set-up should like this:

(set 1) Load autosampler L rack with 28mL cups

Position	Standard
5/45	ST00
5/46	ST01
5/47	ST02
5/48	ST0[illegible]
1/1	CRI
5/42	PQL solution
5/44	ICV solution
5/43	ICB/CCB solution
1/2	ICSA solution
1/3	ICSAB solution
1/4	CRI solution
1/7 - 1/18	CCV solution (for long runs)
	CCB solution

(set 2) Load autosampler (48 position racks):

Position	Name
1	PBW (BATCH #)
2	LCSW (BATCH #)
3	SAMPLE
4	DUPLICATE D
5	SPIKE S
6	SERIAL DILUTION L
7	POST DIGESTION SPIKE
8	SAMPLE2
9	SAMPLE3
10	SAMPLE4
	CCV1
	CCB1
11 .. 20	10 more samples
	CCV1
	CCB1
21 .. 30	10 more samples
	CCV1

	CCB1
31 .. 40	10
	CCV1
	CCB1
41 .. 48,	8 more samples
rack 2, 1 .. 2	2 more samples
	CCV1
	CCB1

NOTE 1: The autosampler assigns the positions of the samples and QC in the order in which they are entered. Modifying an existing run by inserting samples may change the assignments of the samples.

NOTE 2: In order to take multiple uptakes from the same QC cup, the identical name must be entered. This would not allow for the numbering of CCV1/CCB1, CCV2/CCB2, etc. or the suffix of "I" or "F" for ICSA, ICSAB, PQL check solution used in CLP type packages.

7.6 Sample Analysis

7.6.1 Initiate autosampler run. Under the Operation menu, select Analysis, enter the method, press F9 for autosampler run; enter the desired autosampler batch file and press F1, to start operation.

7.6.2 If the samples to be analyzed have been digested then all the calibration standards and quality control solutions used should be prepared using flame water.

7.6.3 Record the analysis sequence, the instrument identification, the date, the analyst's name, the analyst's signature, the time of analysis initiation, and the work order numbers on the bench sheet. Submit a copy of the bench sheet with the raw data.

7.7 Quality Control Requirements

7.7.1 Calibration Curve

All analyses require that a calibration curve be prepared to cover the appropriate concentration range. The calibration curve must be prepared daily with a minimum of a calibration blank and two standards. The curve must have a correlation coefficient of 0.995.

7.7.2 ICV/CCV

The ICV/CCV is run immediately after calibration. The CCV is run after every ten samples or every two hours. The ICV and CCV must be within 10% of the true value. When measurements for any element exceed the control limits the analysis is void for that element. The problem must be corrected and the samples reanalyzed.

Acceptance Criteria
ICV

Element	Control Limits (ppb)	True Value (ppb)
Antimony	360 - 440	400
Arsenic	360 - 440	400
Lead	360 - 440	400
Selenium	360 - 440	400
Silver	36 - 44	40
Thallium	360 - 440	400
Aluminum	4500 - 5500	5000
Barium	360 - 440	400
Beryllium	36 - 44	40
Cadmium	36 - 44	40
Calcium	4500 - 5500	5000
Chromium	360 - 440	400
Cobalt	360 - 440	400
Copper	360 - 440	400
Iron	4500 - 5500	5000
Magnesium	4500 - 5500	5000
Manganese	360 - 440	400
Nickel	360 - 440	400
Vanadium	360 - 440	400
Zinc	360 - 440	400
Potassium	4500 - 5500	5000
Sodium	9000 - 11000	10000
Molybdenum	360 - 440	400
Boron	360 - 440	400
Strontium	360 - 440	400
Titanium	360 - 440	400
Tin	360 - 440	400
Silicon	360 - 440	400

Acceptance Criteria
CCV

Element	Control Limits (ppb)	True Value (ppb
Aluminum	45,000 – 55,000	50,000
Antimony	900 – 1100	1000
Arsenic	900 – 1100	1000
Barium	450-550	500
Beryllium	45 – 55	50
Cadmium	450 – 550	500
Calcium	90,000 – 110,000	100,000
Chromium	450 – 550	500
Cobalt	450 – 550	[illegible]
Copper	450 – 550	[illegible]
Iron	45,000 – 55,000	[illegible]
Lead	450 – 550	[illegible]
Magnesium	90,000 – 110,000	[illegible]
Manganese	450 – 550	[illegible]
Nickel	450 – 550	[illegible]
Potassium	22,500 – 27,500	[illegible]
Selenium	900 – 1100	1000
Silver	45 – 55	50
Sodium	90,000 – 110,000	100,000
Thallium	900 – 1100	1000
Vanadium	450 – 550	500
Zinc	450 – 550	500
Boron	450 – 550	500
Molybdenum	450 – 550	500
Tin	450 – 550	500
Strontium	450 – 550	500
Titanium	450 – 550	500
Silicon	450 – 550	500

7.7.3 ICB/CCB

The ICB and CCB are blank solutions. The ICB must be run immediately after the ICV. A CCB must be run immediately after each CCV. The absolute value of the ICB and CCB measurements should be less than or equal to the PQL. For ACOE project, the absolute value of the ICB/CCB measurements should be less than or equal to the PQL.

Element	PQL (ppb)
Antimony	20
Arsenic	20
Lead	10
Selenium	20
Silver	3
Thallium	30
Aluminum	200
Barium	5
Beryllium	2
Cadmium	6
Calcium	1000
Chromium	5
Cobalt	5
Copper	10
Iron	150
Magnesium	250
Manganese	5
Nickel	10
Vanadium	10
Zinc	20
Potassium	250
Sodium	2500
Molybdenum	5
Boron	15
Strontium	5
Titanium	25
Tin	25
Silicon	50

7.7.4 ICSA/ICSAB

The ICSA and ICSAB must be run at the beginning and end of each analysis run or at a minimum of twice per eight hour shift. ICSAB must be run immediately following ICSA. ICSA contains interferents. ICSAB contains analytes plus interferents. The ICSA analytes results must be within absolute value of their reporting limits. If any element is outside this limit, then the analysis is void for that element. The ICSAB measurements must be within 20% of the true values except for K which must be within 30%. If any element is outside this limit, then the analysis is void for that

element. The problem must be corrected and the element should be reanalyzed.

Acceptance Criteria
ICSA

Element	Control Limits (ppb)	True Value (ppb)
Aluminum	400000 - 600000	500000
Calcium	400000 - 600000	500000
Iron	160000 - 240000	200000
Magnesium	400000 - 600000	500000

Acceptance Criteria
ICSAB

Element	Control Limits (ppb)	True Value (ppb)
Antimony	480 - 720	[illegible]
Arsenic	80 - 120	[illegible]
Lead	40 - 60	50
Selenium	40 - 60	50
Silver	160 - 240	200
Thallium	80 - 120	100
Aluminum	400000 - 600000	500000
Barium	400 - 600	500
Beryllium	400 - 600	500
Cadmium	800 - 1200	1000
Calcium	400000 - 600000	500000
Chromium	400 - 600	500
Cobalt	400 - 600	500
Copper	400 - 600	500
Iron	160000 - 240000	200000
Magnesium	400000 - 600000	500000
Manganese	400 - 600	500
Nickel	800 - 1200	1000
Vanadium	400 - 600	500
Zinc	800 - 1200	1000
Potassium	3500 - 6500	5000
Sodium	4000 - 6000	5000
Molybdenum	800 - 1200	1000
Boron	800 - 1200	1000
Titanium	800 - 1200	1000
Tin	800 - 1200	1000
Strontium	800 - 1200	1000

7.7.5 Linear Range (LR)

The LR (Linear Range) is to verify linearity of each element. The LR must be run at least once during analysis. Any element results above the LR must be diluted and reanalyzed. Specific acceptance range ± 10% of the true value will be used.

7.7.6 PQL (LOWCHECK)

The PQL (LOWCHECK) is to verify linearity at the reporting limit. The PQL (LOWCHECK) is prepared at approximately 5 times the MDL. The PQL must be run at least once during analysis. Advisory acceptance range of ± 20% will be used.

7.7.7 BLK

The BLK are laboratory digested blanks. If any element concentration in the digested blank is above the PQL, then all the samples associated with that blank which have concentrations greater than the PQL and less than ten times the blank concentration must be re-digested and reanalyzed for that element. If any element concentration in the digested blank is less than the negative of the PQL, then all samples associated with that blank must be reanalyzed. For ACOE project, the criteria for BLK is less than or equal to one half the PQL.

Preparation blanks for Navy samples must meet Navy requirements:

- If the concentration of the BLK is greater than the MDL but less than the clients reporting limit, rerun the BLK once. If it is still above the MDL, flag the BLK with a B flag
- If the BLK concentration is greater than the clients reporting limit, but all associated samples are greater than 10 times the blank concentration or less than the reporting limit, rerun the MDL once. If it is still above the reporting limit, it must be noted in the case narrative.
- If the BLK concentration is greater than the client reporting limit and the samples are less than or equal to 10X the BLK concentration (but not less than the reporting limit) the samples must be re-digested and reanalyzed
- If the BLK concentration is less than the MDL, no corrective action is needed.

7.7.8 BKS

The BKS are digested control samples. The BKS measurements must be within laboratory determined control limits. If any element concentration in the BKS is outside the control limits, then all the samples associated with that BKS must be re-digested and reanalyzed. The same spiking levels for the BKS are used for the MS.

In house BKS control limits are generated once a year. BKS recoveries are also checked periodically to identify trends in the digestion/analysis.

7.7.9 Duplicates

One duplicate must be analyzed for each matrix type in each group of 20 samples. If an element concentration is greater than or equal to five times the PQL, then the % RPD should be 20%.

$$\%RPD = \frac{\text{sample} - \text{dup}}{\frac{\text{sample} + \text{dup}}{2}} \times 100$$

If the duplicate falls outside the criteria, it must be noted on the raw data and written in the case narrative.

7.7.10 Matrix Spike

The spike sample analysis is designed to provide information regarding the digestion and methodology used for analysis. One spike is prepared for each matrix type in each batch of samples. If the spike recovery for an element is outside ±25% of the true value, and if the sample concentration corresponding to the spiked sample is less than four times the spike added, then it should be noted in the case narrative and in the raw data. For purposes of calculating the % spike recovery, sample results less than the instrument detection limit reporting limit, should be assumed to be zero.

Spiking Levels

Element	Aqueous (ppb)	Solid (ppb)
Barium	500	1000
Antimony	50	100
Arsenic	50	100
Lead	500	1000
Selenium	50	100
Silver	50	100
Thallium	50	100
Aluminum	5000	10000
Beryllium	25	50
Cadmium	50	100
Calcium	5000	10000

Chromium	250	500
Cobalt	250	500
Copper	250	500
Iron	5000	10000
Manganese	250	500
Nickel	250	500
Vanadium	250	500
Zinc	500	1000
Potassium	5000	10000
Sodium	5000	10000
Molybdenum	25	500
Boron	500	1000
Strontium	1000	1000
Titanium	1000	2500
Tin	250	500
Magnesium	5000	10000
Silicon	5000	10000

7.7.11 Post Digestion Spike

A post digestion spike is analyzed on each batch of digested samples. The post digestion spike should be 10-100 times the MDL. The post digestion spike can be analyzed on a diluted sample if the sample requires dilution. The post digestion spike criteria is 75-125%. If the spike addition is not insignificant. (Sample conc. is not greater than 4x the spike addition)

7.7.12 Serial Dilution

Transfer 2mLs of sample to 8mLs of flame water. One serial dilution is prepared for each sample of each matrix type in each group of samples. If the element concentration is fifty times the reporting limit or greater, then the % difference between the serial dilution and the sample should be 10%.

$$\% \text{ Difference} \quad \frac{\text{sample - dilution}}{\text{sample}} \times 100$$

7.7.13 Internal Standard

The internal standard should be approximately 40ppm. When internal standard is outside control limits of 50% the analysis will be repeated. The problem must be corrected and all samples reanalyzed.

7.7.14 Interelement Correction factor determination (IEC)

OVERVIEW.

Inter-element interference's are false spectral signals arising from other elements in the sample besides the analyte. By measuring the apparent false signal of interfering elements at known concentrations, corrections factors can be determined and applied to unknown samples. These are determined annually or when routine interference check samples reveal the need for further adjustments.

PROCEDURE

Set up, profile, and calibrate the ICP. Introduce clean single element standards at the linear range concentrations. Determine the correction factor using the following equation:

$$\text{(eq 1)} \quad k_1 = \frac{\text{apparent concentration of analyte}}{\text{known concentration of interferent}}$$

IEC's are then verified by introducing solutions of the interferences to determine the effectiveness of the IECs at canceling the apparent concentrations. IEC's are entered into the software controlling the ICP for application to unknown samples.

REPORTING

After all inter-element correction factors have been determined IEC's are entered on CLP forms 11A and 11B

7.8 Hardness by Calculation

The preferred method for determining hardness is to calculate the results of separate determinations of calcium and magnesium.

7.8.1 Calculation

Hardness, mg equivalent $CaCO_3$/L = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]

7.9 Instrument Shut Down

7.9.1 Aspirate flame water for several minutes.

7.9.2 Under Setup menu, select F7 (shutdown). This shuts off the torch and pump windings, goes through a cool down period of 90 seconds before shutting off the water recirculator and gas flows.

7.9.3 After the peristaltic pump stops, disengage the top two cartridges, leaving the tension setting untouched. The bottom cartridge supplies tension to the rinse reservoir and should be kept on to prevent back flowing of the rinse water.

7.9.4 Leave the circuit breaker on the RF power unit behind the instrument on at all times.

7.9.5 Leave the nitrogen purge gas on at all times.

7.10 Trouble shooting and corrective action

7.10.1 Problem: Stable plasma will not start.

Action: Make sure the pump tubing is clamped down [illegible] there are no leaks in the tubing or spray chamber. [illegible] drain line is submerged under [illegible] inches of water in the drain waste vessel. Press [illegible] instrument [illegible]

7.10.2 Problem: Profile peak positioning [illegible] than 0.3 [illegible] position.

Action: ICP may not have reached [illegible] or thermal equilibrium. Check the nitrogen purge [illegible] low, replace nitrogen dewar if empty or low pressure prevents sufficient purging. If purge is sufficient, try re-profiling and recalculate spectrum shifter position. Set new vernier position and verify profile. Record new vernier position in daily maintenance log.

7.10.3 Problem: ICV fails for an element.

Action: (a) The instrument will need to be re-calibrated. (b) The profile may have drifted beyond 0.3 units from zero position. (c) The sample introduction system may have deteriorated since calibration indicating the nebulizer tip, pump windings, etc. may need cleaning or replacement. (d) The internal standard may have run out. (e) the ICV solution or sample introduction system may have been contaminated, perform additional rinse, refill ICV/CCV, and rerun to verify. (f) The calibration standards may need to be remade. (g) IEC's have changed.

7.10.4 Problem: ICB fails for an element.

Action: (a) The instrument will need to be re-calibrated. (b) The profile may have drifted beyond 0.3 units from zero position. (c) The sample introduction system may have deteriorated since calibration indicating the nebulizer tip, pump windings, etc. may need cleaning or replacement. (d) The internal standard may have run out. (e) the ICB solution or sample

introduction system may have been contaminated, perform additional rinse, refill ICB/CCB, and rerun to verify. (f) The calibration standards may need to be remade. (g) The torch is dirty and will need to be cleaned.

7.10.5 Problem: ICSA or ICSAB fails for an element.

Action: (a) The spectrum shifter may need to be re-profiled, (b) the Interelement correction files may need to be changed or (c) new background points may need to be selected and new IEC performed.

8.0 SAFETY

8.1 Equipment

- Lab coat
- Safety glasses
- Gloves

8.2 Potential hazards

8.2.1 All samples and solutions are maintained 5% HCl and may contain high concentrations of metals as well. Safety glasses should be worn to protect the eyes from acid splashes. Gloves and lab coats should be worn to protect the hands and skin from spills or splatter. If any solution comes in contact with the skin, wash the area immediately with plenty of water and notify a supervisor. If any solution is splashed in the eyes, flush immediately and thoroughly in an eyewash basin and contact a supervisor immediately.

8.2.2 The ICP uses high voltage electricity and generates an RF field, so there is a potential risk of electrocution if shielding is circumvented. The TJA ICP has numerous safety interlocks to shut off power to the RF coils if there is a break in the shielding around the coils, if the supply of cooling water is lost, or if there is a loss of argon pressure.

9.0 WASTE MANAGEMENT

9.1 After analysis sample digestates must be held for six months, after which they are disposed of in accordance with the Hazardous Waste Disposal Procedure. For procedure and methods used for disposal refer to Standard Operating Procedures D.1 and D.2.

9.2 All other non hazardous solutions may be washed down the drain with copious amounts of water.

10.0 POLLUTION PREVENTION

10.1 GPL Laboratory operates in a safe manner to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. For more detail on pollution prevention, refer to GPL SOP D.5.

11.0 REPORTING REQUIREMENTS

11.1 The ICP run log must be filled out for each day's operations. The method, date & time of start and end of each run standard sequence and sources, QC sequence and sources, and sequence of samples analyzed and date for preparation batch. In addition, each run must be recorded according to work order tracking numbers, corresponding elements completed, and analyst's initials

11.2 If any maintenance is performed, routine or non-routine, the maintenance log for the affected ICP shall be filled out if service people conduct maintenance on the instrument. The field service report is filed with binder.

11.3 All solutions made must be entered in Solutions Manager program and print out is kept in a notebook in the laboratory.

11.4 Include copy of digestion log with weights and final volume for reviewer.

11.5 Include short narrative on why the run was needed, what problems were encountered, what actions were taken to correct them, and any future actions that will be needed.

12.0 METHOD PERFORMANCE

12.1 For digestion methods MDL limits are obtained by digestion seven spiked replicates the same way as samples and analyzing them MDL is defined as the minimum concentrating of a substance that can be measured and reported with 99% confidence that the value is above zero Precision and accuracy studies are performed once a year at a minimum

13.0 METHOD DETECTION LIMIT

13.1 Method detection limits for this method are listed in the GPL Laboratory Method Detection Limit and Reporting Limit official book.

14.0 DEFINITIONS

14.1 For definitions of terms used in this document, refer to GPL Laboratory SOP G.14.

SOP No: H.12

Title: Cold Vapor Analysis for Mercury in Accordance with SW846 Methods 7470A and 7471A.

1.0 SCOPE AND APPLICATION

1.1 The method detailed in this procedure explains the analysis of mercury in water, soil, sediment and TCLP extracts, by the Manual Cold Vapor Technique in accordance with SW846 methods 7470A and 7471A.

2.0 METHOD SUMMARY

2.1 To quantify both organic and inorganic forms of mercury in water, TCLP extracts, soil and sediment. The sample holding time is 28 days from sample collection. Sample digests containing mercury concentrations greater than the highest calibration standard will be diluted.

3.0 SAFETY

3.1 Gloves, safety glasses, and lab coat must be worn when performing any aspect of the mercury digestion or analysis process.

3.2 Mercury vapor is toxic. Caution should be taken during all phases of the digestion and analytical process. Care should be exercised so that mercury has no chance to be absorbed through the skin or inhaled.

3.3 The acids used to digest mercury are used full strength. Extreme care should be taken so that acid does not spill or splash. Transport samples and empty bottles on one of the 3 high concentration room spill carts. Transport acid using the 4 liter plastic carrying buckets.

3.4 Additional safety equipment includes mercury sponges, acid neutralization media, shoe and leg splash protection, a mercury scrubber, and face shield.

4.0 INTERFERENCES

4.1 Contaminants in the solvents, reagents, glassware and other sample processing hardware. These contaminants lead to discrete artifacts or to elevate baseline in gas chromatograms. All of these materials routinely must be demonstrated by running laboratory method blanks. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of the interferences will vary from source to source.

5.0 EQUIPMENT AND SUPPLIES

5.1 Mercury Digestion Equipment

- 300mL BOD bottles with glass stoppers
- hot plates
- hot water bath trays
- 5000µL pipet with tips (Oxford)
- 1000µL pipet with tips (Eppendorf)
- 100µL pipet with tips (Eppendorf)
- 5mL disposable cups (plastic)
- 100mL graduated cylinders, class A
- balance capable of accurately measuring 0.200 grams (± .001g)
- squirt bottle filled with deionized water
- squirt bottle filled with 2% nitric acid
- squirt bottle filled with 10% hydrochloric acid
- Parafilm squares for mixing standards in volumetric flasks
- thermometer traceable to NIST, alcohol based.
- Bottle top dispensers

5.2 Leeman Labs Automated Mercury Analyzer, Model PS200

5.3 Air source capable of delivering 1 liter of air per minute, argon source.

6.0 REAGENTS AND STANDARDS

- Concentrated Nitric Acid, Trace Metals Grade. Fisher cat. #A509212
- Concentrated Sulfuric Acid, Trace Metals Grade.
- Concentrated Hydrochloric Acid, Trace metals Grade. Fisher cat. #A510212
- Potassium Permanganate solution, 5% w/v. Dissolve 50g Potassium Permanganate to a final volume of 1 liter of distilled water.
- Potassium Persulfate solution, 5% w/v. Dissolve 50g Potassium Persulfate to a final volume of 1 liter of distilled water.

- Stock Mercury solution, 1µg/mL, traceable to NBS standard reference materials. (Source: High Purity Standards, Charleston, SC).

- Stannous chloride (10%). Dissolve 100g of Stannous chloride to 1 liter of 10% HCl. [Leeman requires the use of 10% Stannous chloride in 10% HCl, DO NOT SUBSTITUTE stannous sulfate or sulfuric acid as described in the EPA method.]

- 10% Hydrochloric acid. To a 20L HDPE carboy, add 10L deionized water, then add 2000mL of concentrated hydrochloric acid. Add deionized water to 20L final volume, cap container and mix. Record initials, date of preparation, and lot number of acid on side of carboy.

- Deionized water ASTM Type II or equivalent.

- Sodium chloride - Hydroxylamine sulfate solution - Dissolve 12g of sodium chloride and 12g of hydroxylamine sulfate in deionized water and dilute to 100ml (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate).

- ICV Solution, Laboratory Control Sample, (second source).

- 50% aqua regia digestion solution. To a 1L teflon bottle, add 500mL DI water. Slowly add 125mL conc. HNO_3 and 375mL conc. HCL.

7.0 SAMPLE COLLECTION AND PRESERVATION

7.1 The holding time for mercury is 28 days.

7.2 Samples may be collected in either plastic or glass containers for aqueous samples. At least 500ml should be collected. For soil/solid samples, at least 3 grams should be collected.

7.3 All samples should be stored at 0-4°C

8.0 CALIBRATION AND STANDARDIZATION

8.1 10ppm Hg intermediate stock in 2% HNO_3. Pipet 0.5000ml of 1000ppm Hg stock standard into a 50ml volumetric flask. Add 2% HNO_3 to a final volume of 50ml.

8.2 0.1ppm (100ppb) Hg working solution. Pipet 1ml of 10ppm Hg intermediate stock standard into a 100ml volumetric flask. Add 2% HNO_3 to final volume of 100ml.

Standards for Water Samples

8.3 10.0ppb Calibration standard. Pipet 10ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Transfer into BOD bottle.

8.4 5.0ppb Calibration standard. Pipet 5.0ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Transfer into BOD bottle.

8.5 1.0ppb Calibration standard. Pipet 1.0ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Transfer into BOD bottle.

8.6 0 5ppb Calibration standard. Pipet 0.5ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3. Transfer into BOD bottle.

8.7 0 2ppb CRA standard. Pipet 0.2ml of 100ppb into 100ml volumetric flask. Dilute to volume with 2% HNO_3 Transfer into BOD bottle.

8.8 Calibration blank Add 100ml 2% HNO_3 using a graduated cylinder into BOD bottle.

8.9 ICV working solution (0 1ppm) Pipet 0.100ml of ICV solution (100ppm) into a 100ml volumetric flask Dilute to volume with 2% HNO_3

8 10 ICV check solution (5 0ppb) Pipet 5 0ml of working solution (0.1ppm) into 100ml volumetric flask Dilute to volume with 2% HNO_3. Final concentration of 5ppb. Transfer into BOD bottle

8.11 ICB check solution. Add 100ml 2% HNO_3 using a graduated cylinder. Transfer into BOD bottle.

8.12 Preparation Blank for Water (PBW) Add 100mL deionized water using graduated cylinder into BOD bottle.

8.13 Laboratory Control Sample (LCSW) Add 100mL deionized water using graduated cylinder to BOD bottle. Spike with 1.0mL of 0.1ppm working standard.

Standards for BOD digestion

8.14 Pipet 0.0 2, 0.5, 1.0, 5 0 and 10.0mL aliquots of 0.1ppm Working standard directly into BOD bottle Add compensating volumes of 2% HNO_3 to make 10mL.

8.15 ICV for soils Pipet 5.0mL of 0.100ppm second source and 5.0mL of 2% HNO_3.

8.16 Preparation Blank. Pipet 10.0mL of DI water.

Digestion of Standards. during the digestion, use only 50ml of ASTM type II water during step C.3 for the standards to compensate for the volume of water added in the beginning. Add 50mL of distilled water and 15mL 5% potassium posmanganate solution to each standard bottle. Place in hot batch for 30 minutes. Remove and allow to cool. Add 50mL DI water and 6mL sodium chloride-hydroxylamine HCL.

9.0 METHOD DETECTION LIMIT

9.1 Method detection limits for this method are listed in the GPL Laboratory Method Detection Limit and Reporting Limit official book.

10.0 METHOD PERFORMANCE

10.1 The MDL concentrations listed in the GPL MDL book are generally obtained using organic-free reagent water. Results were also obtained by extracting seven spiked replicates the same way as the samples and analyzing them. MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. Precision and accuracy studies are performed once a year at a minimum. Single operator precision, overall precision and method accuracy were found to be independent related to the concentration of the parameter.

11.0 PROCEDURE (See Figure 1 for flow chart)

11.1 Preliminary Preparations.

11.1.1 Read workorders and test sheets for assigned samples noting which samples are selected for duplicate and spike analysis. Review special instructions and submit sample request form to sample receiving for assigned samples.

11.1.2 Obtain samples from sample receiving and verify the identity of each sample. Record in the Mercury Digestion Log Form the date of digestion, analyst initials and make an entry for each sample assigned (workorder-sample-fraction and client ID) using one line for each sample, standard, quality control check standard, blank, duplicate, spiked sample, and laboratory control sample.

11.1.3 Prepare BOD bottles for each entry by writing with permanent ink on the outside of the bottle the workorder number, the sample number, and fraction--for duplicate of spikes, using "DUP" and "SPK".

11.2 Sample Digestion for Waters/TCLP Extracts

11.2.1 In the metals digestion lab measure 100.0mL of water or leachate sample into a clean, 100mL graduated cylinder and transfer sample into a clean, labeled 300mL BOD bottle. Stopper the BOD bottle, replace onto spill cart.

11.2.2 In the hood, to each bottle, add 5.0mL of concentrated sulfuric acid, 2.5mL of concentrated nitric acid, and 15mL of 5% potassium permanganate solution. Mix sample after each addition. After the first 3 reagents have been added let the samples sit for 15 minutes. If a sample does not retain a purple color after sitting for 15 minutes, add additional

potassium permanganate in 8mL increments until the sample is able to sit for 15 minutes without losing color. Do not add more than 32mL of potassium permanganate to any sample. Record the amount of permanganate added, if additional permanganate was required into the digestion log.

Note: If additional permanganate is added, the final volume must be changed accordingly on the bench sheet for correct final calculation of results.

11.2.3 Add 8mL of 5% potassium persulfate solution to each sample.

11.2.4 Set up water bath and pre-heat to 95°C using a NBS traceable thermometer to check temperature. Cover the pan with the glass marbles or plastic balls. When water bath has reached the correct temperature, record temperature in digestion log, and place bottles in water for 2 hours.

11.2.5 Remove samples from water bath and allow samples to cool to room temperature. Add 6mL of Sodium Chloride-Hydroxylamine Hydrochloride solution and swirl bottle to mix so that all traces of permanganate will be reduced. [Caution: The addition of this solution produces an effervescence which could cause bottle pressure build up and force out the glass stopper. After adding the hydroxylamine to the sample, let the pressure vent off by removing the glass stopper periodically.]

11.2.6 Samples are ready for analysis.

11.3 Sample Digestion for Soils and Sediments

11.3.1 Use an analytical balance to measure a representative 0.500-1.00g, or three separate scoops of approximately 0.2 grams each of soil, or sludge, Laboratory Control Sample, solid or sediment sample into a small weigh boat. Record measurement to 3 significant figures. Wash the sample into a clean, labeled 300mL BOD bottle using a minimum of distilled water dispensed from a squirt bottle. Stopper the BOD bottle. When all samples have been measured, return the unused portion of sample to sample receiving, then transport the measured portion of sample to the high concentration lab.

11.3.2 In the hood, add 10mL 50% aqua regia digestion solution to each BOD bottle. Add 10mL of distilled water to each BOD bottle. Heat sample for 2 minutes at 95°C.

11.3.3 Remove bottles from bath and allow to cool. Add 40mL of distilled water then 15mL of potassium permanganate to each bottle. Heat samples in water bath in hood for 30 minutes at 95°C.

11.3.4 Remove bottles and allow samples to cool to room temperature. Add 50.0mL DI water. Add 6mL of Sodium Chloride Hydroxylamine Hydrochloride solution to reduce the excess permanganate.

11.4 Tuning and Calibration of Instrument PS200.

Soil and water samples each need their own standards and cannot be run under the same standards

11.4.1 Maintenance: change wash bath (daily), change drying tube filled with coarse magnesium perchlorate (daily), check pump tubing (replace weekly), reductant level, and waste vessel.

11.4.2 Change Wash bath: Press F10 to interrupt overnight macro, F9 Utilities, Diagnostics, then select "tip home" with cursor keys and press enter (autosampler tip will move up allowing water bath to be removed). Pour off old wash acid into disposal container, rinse with tap water, clean with soap, fill with 1.1 nitric acid for leaching for 1 hour, rinse with DI water, and refill with 10% HCl acid. Replace water bath and press F1, Instrument, Tip to rinse.

11.4.3 Replace Drying tube: Remove wash bath (see above), Pull off end caps, and remove drying tube. Immerse tube in water to remove unused magnesium perchlorate, discard old quartz wool. Clean tube thoroughly, dry and repack with quartz wool and magnesium perchlorate. Verify that particles of magnesium perchlorate can not enter the small tubing, thereby impeding the flow of gas creating back-pressure. Check pump tubing: Remove cassette from pump housing. Replace tubing on weekly basis.

11.4.4 Run macro "warmstrt": press F2, type "WARMSTRT" and press enter.

11.4.5 Run test optics macro after "warmstrt", Utilities, Diagnostics, select TEST OPTICS using cursor keys, press enter. The readings in microvolts should be within 1000 of each other and both should be above 450000. Imbalances can be adjusted using the aperture adjustment screws located on the cell. If the test optic value for the sample tube is greater than the reference tube, screw in the aperture for the sample tube (bottom screw) to block a portion of light and recheck as necessary until both are within 1000 of each other. Record final readings on instrument use log

11.4.6 Data Storage: Set up file to receive data. Press Data, Folder, enter the name of folder then press enter. A batch name can be used to separate runs within a folder. Press F1, F4 to enter reports submenu, then press H for batcH, at prompt enter new batch name, then press enter. All results will be associated with this name for later retrieval for importing into the laboratory's database.

11.4.7 Instrument Calibration. Load standards onto standards rack, run "CAL6PT" macro, press F2, type CAL6PT, press enter. Instrument will now run standards 1 to 6 in triplicate. If curve linearity is greater than .998, and the deviation of blank is within 0.1ug/L, press A to accept the curve and press F3 to print out calibration curve.

11.4.8 Verify calibration with check standard and check blank. Load ICV solution into standard rack position C2, and check blank into C3. Press F6, then press 2 to run check standard 2 (ICV), then press F6, 3 to run check blank. If results are within control limits of 80 -120%, set frequency of the check samples to 10% and the instrument will automatically run check sample 2 and then check sample 3 every 10 samples.

11.4.9 Rack Entry: Press Autosampler, Rack Entry, type in initials, year, month, day, and a letter in the following format XXMMDDA. (If more than one rack will be prepared, use XXMMDDB.) At the prompt reply Y for open rack file and begin entering sequence of tubes. Note that the weight and volumes fields will not be used (size and volume will be entered into post-run file.)

11.4.10 Set up autosampler. Press F1, Autosampler, Set up, press 1, then enter name of rack file for rack 1, then enter starting position and ending position. Press F8, then F8 again to begin autosampler run.

Trouble Shooting Guide: Refer to Leeman Labs Manual.

12.0 DATA ANALYSIS AND CALCULATION

12.1 In addition to the accurate reporting and handling of raw data, there are records that need to be maintained for internal auditing purposes.

12.1.1 Before analysis is completed, record on the raw data the date of analysis, the analyst, the Mercury standard's source, lot number, and GPL ID, the ICV's number, and GPL ID, the LCSS's number and GPL ID, a list of the cases included in the run, and the instrument upon which the analysis was performed. Note the source for the spike used in the matrix spike sample and % Recovery for the spike in the raw data.

12.1.2 Complete the Bench Sheet for Mercury with the following information: Instrument ID, Date of analysis, Analyst name and signature, Time analysis was initiated, case and SDG, work order numbers, sample sequence run, dilution factors and comments.

12.1.3 Complete the Instrument Use Log with the following information: Date, Method, Case, Analyst and Comments.

12.1.4 If maintenance or repair was required on the instrument, all relevant information must be recorded in the Maintenance Log. This Log will be maintained with all field service reports for each instrument.

13.0 QUALITY CONTROL

13.1 Any results that exceed the highest calibration standard are diluted and reanalyzed. (LR = highest calibration standard)

13.2 The mercury auto-analyzer is capable of detecting parts per billion levels of mercury when optimized. However, the laboratory reports lowest standard concentration level.

13.3 Calibration standards must be prepared fresh daily from stock standards. The deviation of each standard must be within 5% of the standard's concentration or the run must be terminated and the instrument recalibrated. These % criteria does not apply to calibration standard of the CRDL 0.2ppb. The correlation coefficient must be ≥ .995 or the run must be terminated and the instrument re-calibrated.

13.4 Initial Calibration Verification Check solution. An ICV solution is prepared from an independent standard as the calibration standards are prepared. This solution is then digested with the samples and is the 1st check standard to be run. If recovery is outside 90-110% window, the run terminates. Recalibrate and rerun the ICV and ICB.

13.5 Continuing Calibration Check solution. The ICV solution is used as the CCV solution. Window of acceptance for ICV is 90-110%. Window of acceptance for CCV is 80-120%.

13.6 Initial and Continuing Blank Solution. A blank solution, separate from the calibration blank, is digested with the standards and analyzed at after each ICV and CCV. Criteria is ± 0.2ug/L.

13.7 PQL solution. A solution of 0.2ug/L Hg is prepared as calibration standards are being prepared and is analyzed at the beginning of the run following the ICB. Criteria equals 80-120%.

13.8 Preparation Blanks are digested exactly as the samples. The same type of container, utilization of the same amount of reagents, and are assigned to the same digestion batch. The blanks are placed in sequence every twenty samples. Criteria is ± 0.2ug/L.

13.9 Laboratory Control sample. A blank solution is spiked at 1.0ug/L to check the spiking procedure and the digestion process. Acceptance criteria is based on statistical control charting for warning limits.

13.10 Spike Sample. 0.5 - 1.0g of sample is spiked with 1.0mL of 0.1ppm Hg standard before addition of reagents or digestion. One spike is prepared every 20 samples of the same matrix. If the matrix spike is outside 75-125% criteria a post digestion spike must be analyzed (see 8.11). It also must be noted in the case narrative. If the sample is sufficiently high enough, a serial dilution should also be performed when the matrix spike is outside criteria to detect interferences.

13.11 Post digestion spike - This is performed if the matrix spike is outside the criteria. The post digestion spike should fall within the midrange of the calibration curve and should be within 85-115%. If the post digestion spike is outside criteria and the sample result is above the reporting limit an MSA should be performed to quantify the result. The MSA should be used for all samples of similar matrix within the batch.

13.12 Serial Dilution - A serial dilution is performed if the matrix spike is outside criteria if the sample is sufficiently high > 1ug/L. Dilute the sample 1:4 by pipetting 5mL of digested sample into a sample cup and adding 15ml of blank. The percent difference should be 10% or less. If the serial dilution is outside criteria an MSA should be performed to quantify the result. The MSA should be used for all samples of similar matrix within a batch.

13.13 MSA - An MSA is used to quantify results if the matrix spike and post digestion or serial dilution fall outside criteria. To perform an MSA, pipette 5ml of digested sample into four sample cups. Spike the second, third and fourth cups with 1/2, 1 & 1 1/2 times the unspiked sample concentration then add compensating water to bring all cups at same volume. For example, if the one sample concentration is 2ppb spike it with 1/2 & 2ppb respectively. Perform a linear regression to quantify the result using the four points. The correlation coefficient should be [illegible]. If the correlation coefficient is <0.995, rerun the MSA once.

13.14 Duplicate ICPs: duplicate every twenty samples will be performed. The duplicate is digested before addition of any reagents or digestion.

14.0 DISPOSAL REQUIREMENTS

14.1 Collect all waste acid, samples, and standards into 20 liter plastic carboys or similar vessels and transport to waste disposal when container is 3/4 full for pour-off into 55 gallon drums (lined with polyethylene).

14.2 The main disposal concern of mercury digestates is the corrosivity and toxicity characteristics of mercury. The content of the waste can be as high as 30% acid. Varying concentrations of mercury will be present in the digestates and will be determined by waste disposal characteristic procedures prior to release to a disposal company.

15.0 POLLUTION PREVENTION

15.1 GPL Laboratory operates in a safe manner to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. For more detail on pollution prevention, refer to GPL SOP D.5.

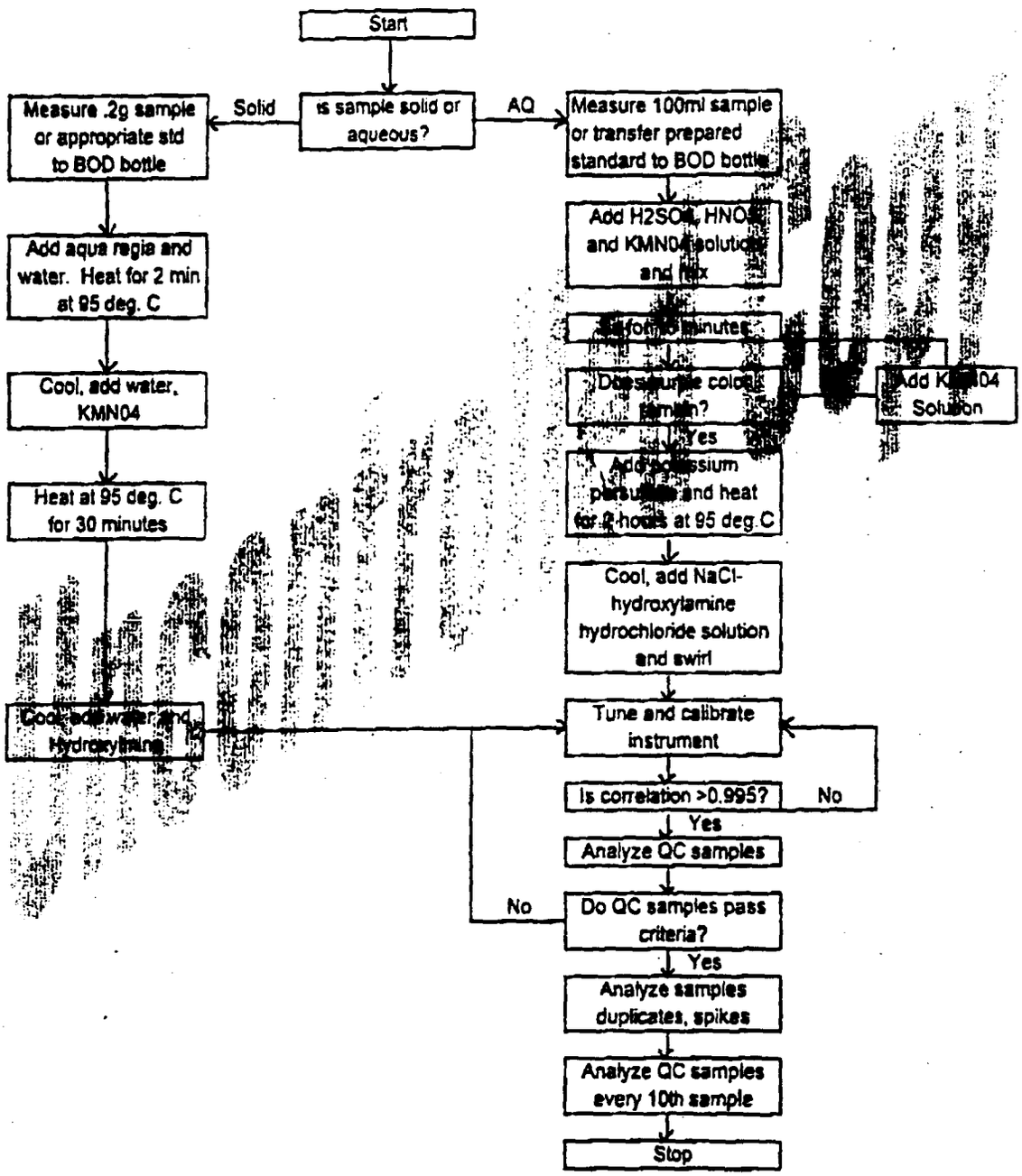
16.0 DEFINITIONS

16.1 For definitions of terms used in this document, refer to GPL Laboratory SOP G.14.

17.0 REFERENCES

- SW846 method 7470A anc 7471A.
- Leeman Labs PS200 Manual, Leeman Labs, Inc., Lowell, MA, Part No. 110-00047, Serial No. Hg-3045.

Figure 1
Procedure Flow Chart



Pace Analytical Services, Inc.
1700 Elm Street, Suite 200
Minneapolis, MN 55414

Phone: 612.607.1700
Fax: 612.607.6444

STANDARD OPERATING PROCEDURE

Sample Receipt and Check-In

SOP NUMBER	MN-C-702-M
REVISED BY	Andrea Nord
EFFECTIVE DATE	Date of final signature
REVIEW DATE	March 27, 2004
SUPERSEDES	MN-C-702-L

APPROVAL

Laboratory Manager	03/27/02 Date
General Manager	3/27/02 Date
Quality Assurance Officer	27 MAR 02 Date

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I. PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to establish a uniform and efficient system for the receipt of samples into the laboratory.

II. SCOPE AND APPLICATION

The policies and procedures contained in this SOP are applicable to all Pace Analytical Services, Inc. personnel.

III. SUMMARY OF METHOD

Not Applicable.

IV. INTERFERENCES

Not Applicable.

V. SAFETY

A. The toxicity or carcinogenicity of each reagent used in this laboratory has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials

B. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals. A reference file of Material Safety Data Sheets (MSDS) is made available to all personnel involved in the chemical analysis. The laboratory has a formal safety plan.

C. MSDS sheets are located at the front desk and should be consulted prior to handling samples and standards.

D. The toxicity or condition of samples received by the laboratory is unknown. Therefore, always wear appropriate personal protective equipment to control exposure to hazards. (Safety glasses, Gloves, Safety shoes, Lab coats)

VI. DEFINITIONS

A. Analyte – The specific entity an analysis seeks to determine.

B. Duplicate Sample – A second aliquot of the same sample that is treated the same as the original sample in order to determine the precision of the method.

C. Environmental Sample – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required. Environmental samples can generally be classified as follows:

Surface and Ground Water

Drinking Water – Delivered (treated or untreated) water designated as potable water.

Water/Wastewater – Raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents.

Sludge – Municipal sludges and industrial sludges.

Soil – Predominately inorganic matter ranging in classification from sands to clays.

Waste – Aqueous and non-aqueous liquid wastes, chemical solids, and industrial liquid and solid wastes

D. EPIC – LIMS developed by Pace Analytical (Environmental Project Information Control)

E. Equipment Blank – Special type of field blank used primarily as a check on equipment decontamination procedures. After decontamination, the sampling equipment is rinsed in DI water and the water collected for analysis.

F. Holding Time – The elapsed time from the date/time of sample collection by the field personnel until the date/time of its processing/analysis. Holding time requirements are dictated by the method or QAPP.

G. LIMS – Laboratory Information Management System.

H. Quality Assurance – A system of policies and procedures whose purpose is to ensure, confirm and document that the product or service rendered fulfills the requirements of Pace Analytical and it client. Quality Assurance includes quality planning, quality control, quality assessment (auditing), quality reporting and corrective action.

I. Replicate Samples – Samples collected at the same time, from the same place, for the same analysis, as the original sample in order to determine precision between samples.

J. Trip Blank – this blank is used to detect sample contamination from the container and preservative during transport and storage of the sample. A cleaned sample container is filled with laboratory pure water; and preservative used in the sample is added; and then the blank is stored, shipped, and analyzed with its group of samples.

VII. RESPONSIBILITIES AND DISTRIBUTION

A. PERSONNEL

1. All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

2. Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

B. LABORATORY MANAGER/SUPERVISOR

1. The laboratory manager/supervisor is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

2. The laboratory manager/supervisor is responsible for performing an annual review of this SOP and reporting any required revisions to the Quality Assurance Office.

C. QUALITY ASSURANCE OFFICE

1. The QA Office is responsible for conducting laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Management.

2. The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

3. The QA Office is responsible for maintaining the original and complete distribution records.

D. REVISIONS

1. This SOP will be reviewed on a biennial basis at minimum, and any required revisions will be incorporated.

VIII. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Not Applicable.

IX. EQUIPMENT AND SUPPLIES

Not Applicable.

X. REAGENTS AND STANDARDS

Not Applicable.

XI. CALIBRATION

Not Applicable.

XII. PROCEDURE

All of the following procedures are applicable to Sample Receiving occurring on any shift of any calendar day.

Client Profiles should be entered into the Laboratory Information Management System, (LIMS) prior to sample receipt (refer to EPIC user manual). This will expedite the check-in process and will allow for more timely distribution of samples into the analytical areas.

A. SAMPLE ACCEPTANCE

1. The Client Services Technician will record the client's name, quantity of coolers sent, and the date and time of receipt for every client/cooler that arrives at this facility in the Cooler Receipt Logbook (see Attachment 9).

2. The Client Services Technician will examine the shipping container, determine if custody seals are intact, and will record any damage upon receipt, if applicable. Any damage noted must be recorded on the Corrective Action Report (CAR). See attachment 3.

3. The Client Services Technician will open the shipping container under a fume hood.

4. The Client Service Technician will review the Chain of Custody (see Attachment 2) to ensure that the sample identification, the location, date and time of collection, collector's name, preservation type, and sample type are clearly stated.

5. The Client Service Technician will compare the Chain of Custody to the actual sample bottle labels. Typically, the sample bottles are lined up under the fume hood by sample identification and bottle type. Any instances where the COC does not match the actual sample bottles, a CAR must be filled out and submitted to the project manager. The project manager must contact the client immediately and document any information.

B. SAMPLE RECEIPT

If the Client Services Technician identifies any deviation to the following observances; a CAR must be completed to document such deviance.

1. The Client Services Technician will open the shipping container under a fume hood and will determine the temperature, presence, and condition of the samples. These observations will be noted as described below.

2. The following observations will be recorded on the COC upon arrival. The Client Service Technician who receives the shipment must sign the COC and note the date and time of receipt.

   a) Temperature:

      1) An Infrared thermometer will be used to determine the temperature of the temperature blank or sample by passing the thermometer over the surface of the container. The temperature will be recorded on the COC, if the temperature is not 4 ± 2 °C a project manager will be contacted immediately. If the temperature of the blank or sample cannot be determined because it is frozen, "frozen" will be written for the temperature.

      2) Samples from the state of Wisconsin must be documented whether the samples are on ice. This should be noted if the temperature is not 4 ± 2 °C.

      3) Samples that are hand delivered to the laboratory immediately after collection may not be at 4 ± 2 °C. In these

cases, the samples shall be considered acceptable if the chilling process has begun such as arrival on ice. Such instances must be noted on the COC.

4) Certain clients have waived the regulatory temperature requirement for the samples that they have collected. A list of these clients, which is updated as needed, is located in the sample receiving area and eliminates Pace Analytical from having to complete a CAR for temperature. These clients have also waived Pace Analytical from any and all responsibility for samples that were not received within the temperature range of 4 ± 2 °C.

b) Sample pH, preserved water sample, non-volatile containers.

1) With the exception of Diesel Range Organics (DRO) analysis bottles; a new disposable pipette will be used to withdraw a small portion of sample from the container. The aliquot will be dispensed on a sample pH strip. If the pH does not fall within the range specified by the Pace Analytical/EPA Methods Reference Chart, see Attachment 9; the discrepancy will be indicated on the CAR, see Attachment 3.

2) With the exception of Diesel Range Organics (DRO) analysis bottles; if the pH is-out of acceptable range, the pH will be adjusted with the recommended volume of the appropriate acid or base, as determined by the Pace Analytical/EPA Methods Reference Chart, and will be recorded on the CAR. The technician performing the adjustment to the sample will complete the required information on a Preservative Added label (see attachment 5) and will label the sample container(s) that needed adjustment. If the adjusted pH does not fall within the accepted range after the addition of more acid or base, this fact will also be noted on the CAR and the PM will be notified.

3) Certain acid or bases are required as preservatives for given analyses. Consult the Pace Analytical/EPA Method Reference Chart to determine if the correct preservative was used for the requested analyses. If not, this will be documented on the CAR and the PM will be notified.

c) Container Type

Sample containers will be selected and utilized based upon method requirements for each specific analysis based upon the Pace Analytical/EPA Methods Reference Chart.

d) Container Condition

Sample containers will be examined for any breakage or leakage. The bottle type for each sample that is broken, leaking, or preserved incorrectly for the analyses required will be noted on the CAR and the PM will be notified. The broken bottles will be placed in an container designed for broken glass an will be disposed of properly.

e) Sample Volume

1) The Pace Analytical/EPA Methods Reference Chart will be consulted for required sample volumes. Any significant deficiencies in volume will be documented on the CAR and the PM will be notified.

f) Headspace (Water, volatile containers)

1) The presence of headspace for samples submitted for volatile analysis will be noted on the CAR and the PM will be notified.

g) Hold Time

1) The Pace Analytical EPA Methods Reference Chart will be consulted for required sample hold times for requested analyses. Any deficiencies in holding time will be documented on the CAR and the PM will be notified.

h) All correspondence with the client must be fully documented by the project manager.

4. For Federal Programs, a Sample Condition Upon Receipt (SCUR) form will be completed by the Client Services Technician. (Attachment 4)

C. SAMPLE CHECK-IN

1. The Client Services Technician will enter samples into the LIMS as outlined in the EPIC users Manual.

2. Each sample will be given a unique laboratory identification. All samples received from a site will be given a unique laboratory project number by the LIMS.

3. The Sample Receipt Form (SRF) will be printed from EPIC.

4. The COC, SRF, SCUR (if applicable), along with any other correspondence received with the shipment will be included in a file folder and placed in the corresponding PM's mail box, which is located in the sample receiving area.

5. Samples are stored in the appropriate cooler according to MN-C-701.

6. If, for any reason, a sample, group of samples, etc. can not be checked into EPIC on the same business day, the sample, group of samples, cooler, tray, etc. must be logged into the Outstanding Projects/On Hold Logbook (see Attachment 7).

7. A Sample On Hold Worksheet (see Attachment 8) must be filled out for all samples a client has requested to be put on hold on a semi-permanent or permanent basis. These samples must also be logged into the Outstanding Projects/ On Hold Logbook. The client requesting the sample analyses to be put on hold must be communicated to the client service technician via the PM or the client themselves.

8. USDA Regulated soils and /or foreign soils must be separated from all other samples and then incinerated. The sample receiving technician must put a "Special Handling" sticker (see Attachment 10) on all sample containers associated with the USDA regulated soil samples (see attachment 11) for further handling procedures.

XIII. QUALITY CONTROL

Not Applicable.

XIV. METHOD PERFORMANCE

The analyst should read and understand this SOP with documentation maintained in his/her training file.

XV. POLLUTION PREVENTION AND WASTE MANAGEMENT

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. The quantity of chemicals purchased should be based on expected usage during its shelf life and 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 Society's Department of Government Regulations and Science Policy, 115 16th Street NW, Washington, DC 20036, (202) 872-4477.

VII. REFERENCES

Contract Lab Program (CLP) Statement of Work for Organic and Inorganic Analyses, 3/90 Revision

USEPA CLP User's Guide, 12/88 Revision

EPIC Users Manual

Pace Analytical SOP, MN-C-701, Sample Storage and Disposition

Pace Analytical SOP, MN-P-001, Corrective Action Reports

Pace Analytical SOP, MN-L-103, Sample Custody

Pace Analytical SOP, MN-Q-208, Preservation, Labeling, and Shipment of Sample Containers

Pace Analytical SOP, MN-L-101, Documentation in the Laboratory

Pace Analytical SOP, MN-C-701, Sample Storage and Disposition

NELAC Standards, Quality Systems, Rev.512.5, November 10,1999.

ATTACHMENT 1

SRF

Pace Analytical Services, Inc.
Minnesota
Sample Receipt Form

Report to Address:

Phone:
FAX:

Line Item Descriptions:
[1] TSS.TDS.COD.BOD.T.Phos

Client P O No
Phone (612)607 6378
Project Manager Andrea Aamitz
Client Project ID Mill Effluent 1557

Lab Project No:
Project Deliverables Type: Pace Level B
Project Report Due Date : 12/15/00
Profile: 10

Lab Smp No: Client Smp ID MILL EFFLUENT Collected Date: 11/30/00 07:00
Proj Smp No: Matrix Water Smp Type: PS Line Item: 1 Received Date: 12/01/00 10:30

PARAMETER	METHOD	UNIT PRICE	WR	SPL	%
Total Suspended Solids	EPA 160.2	$			0
Biochemical Oxygen Demand 5 d	SM 5210B	$			0
	Sub Total - Sample 102425097	$			
	Grand Total - Project 1039342	$			

Unit pricing above does not reflect associated shipping, bottle, sample disposal and other miscellaneous charges.
Prices are subject to change without notice. Contact your Project Manager for further information.

Sample Receipt and Check-in
Pace Analytical Services, Inc.
MN-C-702-M

ATTACHMENT 2
COC

Pace Analytical™
www.pacelabs.com

CHAIN-OF-CUSTODY / Analytical Request Document

The Chain-of-Custody is a LEGAL DOCUMENT. All relevant fields must be completed accurately.

616700

Page: of

Section A — Required Client Information:

Company:
Address:
Phone: Fax:

Section B — Required Client Information:

Report To:
Copy To:
Invoice To:
P.O.
Project Name:
Project Number:

Client Information (Check quote/contract):
Requested Due Date: *TAT:

* Turn around times less than 14 days subject to laboratory and contractual obligations and may result in a Rush Turnaround Surcharge.
Turn Around Time (TAT) in calendar days.

Section C — To Be Completed by Pace Analytical and Client

Quote Reference:
Project Manager:
Project #:
Profile #:
Requested Analysis:

Section D — Required Client Information:

SAMPLE ID
One character per box.
(A-Z, 0-9 / , -)
Sample IDs MUST BE UNIQUE

Valid Matrix Codes

MATRIX	CODE
WATER	WT
SOIL	SL
OIL	OL
WIPE	WP
AIR	AR
TISSUE	TS
OTHER	OT

ITEM #	SAMPLE ID	MATRIX CODE	DATE COLLECTED mm / dd / yy	TIME COLLECTED hh mm a/p	# Containers	Preservatives: Unpreserved	H_2SO_4	HNO_3	HCl	NaOH	$Na_2S_2O_3$	Methanol	Other	Remarks / Lab ID
1														
2														
3														
4														
5														
6														
7														
8														
9														
10														
11														
12														

SHIPMENT METHOD	AIRBILL NO.	SHIPPING DATE	NO. OF COOLERS	RELINQUISHED BY / AFFILIATION	DATE	TIME	ACCEPTED BY / AFFILIATION	DATE	TIME

SAMPLE CONDITION

Temp in °C	
Received on ice	Y/N
Sealed Cooler	Y/N
Samples Intact	Y/N

SAMPLE NOTES

Additional Comments:

SAMPLER NAME AND SIGNATURE
PRINT Name of SAMPLER:
SIGNATURE of SAMPLER: DATE Signed (MM / DD / YY):

ORIGINAL

SEE REVERSE SIDE FOR INSTRUCTIONS

Form COC01 Rev 0601

ATTACHMENT 3
SAMPLE RECEIPT CORRECTIVE ACTION REPORT

Pace Analytical™

Pace Analytical Services, Inc.
1700 Elm Street, Suite 200
Minneapolis, MN 55414
Phone 612 607 1700
Fax 612 607 6444

SAMPLE RECEIPT CORRECTIVE ACTION REPORT # _____

Description of Discrepancy

Project Manager _____ Project Number: _____

Client: _____ Analysis: _____

Sample(s) Affected: _____

Matrix: ▯ Soil/Solid ▯ Water ▯ Air/Wipe ▯ Other_____

Description of Event (Attachments may be included):

▯ 11. Login Error ▯ 12. Mislabeled Bottles by Pace ▯ 13. Mislabeled Bottles by Client

▯ 14. Incorrect COC ▯ 15. Broken Bottles ▯ 16. Preservation ▯ 17. Temperature

▯ 18. Insufficient Hold Time ▯ 19. Missing Bottles ▯ 20. Missing COC ▯ 21. Other_____

Discussion of Known or Suspected Cause: _____

Corrective Actions Taken (Include date, person, and action):_____

Initiator: _____ Date: _____

Original to Project Manager

Project Management

Client Contacted: ▯ Yes ▯ No Contact: _____
Date:_____ Time:_____

Response/Action: _____

Project Manager Signature:_____ Date: _____
Copy included in project folder: ▯ Yes

Quality Assurance

Discrepancy Resolved: ▯ Yes ▯ No
Comments: _____

Quality Assurance Signature: _____ Date: _____
Original in QA file

Doc56qs, 12/00

ATTACHMENT 4
SAMPLE CONDITION UPON RECEIPT FORM (SCUR)

Pace Analytical™

Sample Condition upon Receipt

Pace Analytical Services, Inc.
1700 Elm Street, Suite 200
Minneapolis, MN 55414
Phone: 612.607.1700
Fax: 612.607.6444

PACE Project # _____ Client: _____
Rec. By: _____ Date Rec.: _____

Custody Seals: Present / Absent Intact / Broken Received by: Fed Ex Courier UPS

Temperature of Blanks upon Arrival (If not 4.0 +/- 2.0 Deg C LIST the affected samples on a SEPARATE sheet and staple that sheet DIRECTLY to this sample condition upon receipt form.

Cooler ID:					
Temp. (Celsius):					

☐ Temperature Blank not present, condition of coolant is: _____

Yes	No		
O	☐	1	Short holding time analyses requested Short Hold Analyses: _____
O	☐	2	Sampled four or more days prior to receipt (If "yes", contact supervisor and PM immediately) Earliest date of sampling: _____
O	☐	3	Rush Due Date (one week or less) requested. (If "yes", contact supervisor and PM immediately) Due Date: _____
O	☐	4	Sample Containers are intact.
☐	O	5	Samples Correspond to Client Documentation. (Note Discrepancies below)
☐	O	6	Samples are properly preserved. (See "Preservation Record" for preserved, non-VOA containers)
☐	O	7	VOA samples are free of head space. (List Client Sample Descript. and # of containers with headspace)
☐	O	8	Sample volume appears sufficient.

Notify Project Manager IMMEDIATELY with ANY questions or concerns.

Project Manager Review: _____ Date: _____ Comments: _____

F002ES.xls(5/98)

ATTACHMENT 5
PRESERVATIVE ADDED LABEL

Preservative Added
Type_____, _____mL.

Date_____ Initials_____

ATTACHMENT 6
SAMPLE LABEL

102430832 Cont CO 1of1
Loc 1

1039473-001 Col 12/04/00

ATTACHMENT 7
OUTSTANDING PROJECTS/ON HOLD LOGBOOK

Pace Analytical™
www.pacelabs.com

Pace Analytical Services, Inc.
1700 Elm Street, Suite 200
Minneapolis, MN 55414
Phone: 612.607.1700
Fax: 612.607.6444

OUTSTANDING PROJECTS/CHAIN OF CUSTODY

	Client	PM	# of Coolers/Trays	Date/Time IN	Initials	Date/Time OUT	Initials	Hold?
241								
242								
243								
244								
245								
246								
247								
248								
249								
250								
251								
252								
253								
254								
255								
256								
257								
258								
259								
260								
261								
262								
263								
264								

ATTACHMENT 8
SAMPLE ON HOLD WORKSHEET

Samples on Hold

Client:_____

Project Manager:_____

Date Samples were Received:_____

Logbook # _____

Initiator:_____

Project Number (if applicable)_____

Do not dump !

ATTACHMENT 9
COOLER RECEIPT LOGBOOK

COOLER RECEIVING LOGBOOK

Date	Shipper	Client	Number of Coolers	Time of Delivery

Reviewed by: ______________

Date: ______________

ATTACHMENT 10
SPECIAL HANDLING STICKER

ATTACHMENT 11
FOREIGN SOIL POLICY

Procedure for Handling USDA Regulated Soils

All samples arriving from foreign countries or regulated areas within the United States will be treated according to the specific protocol outlined in this document. All employees handling USDA regulated soils will follow this protocol explicitly. Failure to do so is in direct contradiction to Pace Analytical Services, Inc.'s policies set forth to ensure compliance with all regulatory agencies. The general procedure for handling special soils is as follows:

1. The Project Manager of the specific project containing the regulated soils will distribute a copy of the chain of custody to the section supervisors. The chain of custody will indicate the soil samples are to be handled as special waste.

2. Upon arrival at this facility, neat samples will be labeled with a sticker "SPECIAL HANDLING".

3. The samples will be segregated within the sample storage areas. A separate shelf will be labeled with a sign reading "USDA Regulated Soils"

4. Disposable products used to handle the neat samples will be separated from our solid waste stream and placed into bags or five gallon pails labeled "SPECIAL WASTE." Disposable products include, but are not limited to: gloves, paper towels, weigh boats, tongue depressors, etc.

5. After proper sample storage has expired, the samples and all disposable products will be collected in fifty five gallon steel drums. These drums will be incinerated.

If you have any questions concerning this procedure contact your immediate supervisor or Safety Committee member!

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STANDARD OPERATING PROCEDURE

Preparation and Analysis of Samples for the Determination of Dioxins and Furans by USEPA Method 8290

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APPROVAL

Laboratory Manager — Date: 6-5-02

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I. PURPOSE

To describe the standard operating procedure for the preparation, analysis, processing and reporting of samples for the determination of dioxins and furans using USEPA Method 8290.

II. SCOPE AND APPLICATION

A. Stable isotopically labeled analogs of 15 of the PCDDs and PCDFs are added to each sample. Samples containing coarse solids are prepared for extraction by grinding or homogenization. Water samples are extracted in separatory funnels. Soils and other finely divided solids are extracted using Soxhlet extraction apparatus.

B. After extraction, $^{37}Cl_4$-labeled 2,3,7,8-TCDD may be added to each extract to measure the efficiency of the cleanup process. Sample cleanup may include back extraction with acid and/or base, alumina, silica gel, and activated carbon chromatography. HPLC can be used for further isolation of the 2,3,7,8 isomer or other specific isomers or congeners.

C. Samples are spiked with two labeled recovery standards which are used to determine the portion of the analytes and internal standards which survived the extraction and enrichment processes. The extracts are then analyzed using high resolution gas chromatography/high resolution mass spectrometry to determine the concentration of PCDDs and PCDFs present in the samples.

D. This procedure is limited to the analysis of the dioxin and furan compounds listed in the body of this method.

E. The accuracy of the method can be affected by matrix interferences, especially for non-isotope dilution analytes.

III. SUMMARY OF METHOD

Method 8290 was written for use on water, sludge, soil, fly ash, tissue, and waste materials. This method can be applied to most other matrices as well.

IV. INTERFERENCES

A. Most samples analyzed for PCDD/PCDF content contain other organic compounds that will interfere with or contaminate the mass spectrometric instrumental system. Therefore, after initial extraction, extracts are taken through the enrichment steps outlined in the "Extract Enrichment" section of this procedure. Exceptions to performing the optional enrichment step of acid and carbon column cleanup steps may be made with consultation of the project manager and are usually limited to water matrices.

B. Matrix interferences may be caused by contaminants (particularly chlorinated biphenyl ethers) co-extracted from the sample and will vary considerably from source to source. These biphenyl

ethers rearrange in the mass spectrometry source to form dibenzofurans.

C. Some samples may contain levels of interfering compounds which overload the analyte enrichment columns. Consult the project manager for alternate procedures should this occur.

D. Rigorous glassware cleaning techniques must be used and method blank data must be monitored to evaluate the effectiveness of the glassware cleaning techniques.

E. HPLC grade solvents should be used for extractions. Solvents having new lot numbers should be screened for contamination prior to use by analyzing a solvent blank by the applicable analytical methods.

F. Raw data from all blanks, samples, and spikes are evaluated for interferences. Determine if the source of interferences is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

G. If chromatographic interferences are present, the height from the smaller signal of the pair is used along with the theoretical ratio to determine the height of the second ion. These values are then used to calculate the estimated maximum concentration which is then reported as the detection limit.

H. Some interferences may be reduced by analysis of a dilution of the extract.

V. 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 health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials

B. Each laboratory 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) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advised.

C. MSDS sheets are located at the front desk and should be consulted prior to handling samples and standards.

D. The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Therefore, all PCDDs and PCDFs will be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and who understand the risks associated with this procedure.

E. Neat PCDDs and PCDFs require the use of respirators and are not to be handled in the laboratory.

F. Protective equipment must be worn when working with standards or samples under this procedure. This includes safety glasses, laboratory coat, and throwaway plastic gloves. Plastic sleeves, aprons and other protective equipment are also readily available if needed. All steps of this procedure must be performed in a properly operating fume hood except those noted.

G. All personnel performing any part of this procedure must be properly trained in removing contaminated materials and properly disposing of them. This includes an awareness of personal hygiene as it pertains to the laboratory, personal actions as they affect coworkers, etc.

H. All samples analyzed at the Minneapolis chemistry facility are held until analytical results have been reported. Samples containing PCDD/PCDFs above the allowable levels are labeled, segregated, and disposed of by personnel trained in handling toxic waste. Similarly grossly contaminated waste items including pipette tips and other laboratory equipment are segregated, collected in lined waste containers, properly labeled, and disposed of in accordance with hazardous waste regulations.

I. Laboratory staff will wipe down a representative area of specified fume hoods at least annually using pre-sterilized gauze and hexane. These wipes will be analyzed according to this method to ensure that good laboratory practices are observed at all times. The results of the wipes will be archived for reference.

VI. DEFINITIONS

A. Accuracy – The degree of agreement between a measured value and the true or expected value.

B. Aliquot – A measured portion of a sample taken for analysis.

C. Analyte – The specific entity an analysis seeks to determine.

D. Batch – A grouping of no more than twenty samples of similar matrix which are prepared and/or analyzed together with the same method and the same lots of reagents within the same time frame, as designated by the method.

E. Calibration – The process of establishing the relationship between instrument response and known, traceable quantities of analytes of interest.

F. Calibration Check – Verification of the ratio of instrument response to analyte amount. A calibration check is done by analyzing the analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards.

G. Continuing Calibration – The process of analyzing standards periodically to verify the maintenance of calibration of the analytical system.

H. Control Chart – A graphical representation of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control.

I. Control Limit – A range within which specified measurement results must fall to signify compliance. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that nonconforming data be investigated and flagged.

J. Dry Weight – The weight of a sample based on percent solids. The weight after drying in an oven at a specified temperature.

K. Duplicate Sample – A second aliquot of the same sample that is treated the same as the original sample in order to determine the precision of the method.

L. Environmental Sample – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required. Environmental samples can generally be classified as follows:

Surface and Ground Water

Drinking Water – Delivered (treated or untreated) water designated as potable wate

Water/Wastewater – Raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents.

Sludge – Municipal sludges and industrial sludges.

Soil – Predominately inorganic matter ranging in classification from sands to clays.

Waste – Aqueous and non-aqueous liquid wastes, chemical solids, and industrial liquid and solid wastes.

Tissue – any animal tissue, i.e. fish or other marine animals

Ash – Predominately from incineration

M. Field Blank – A quality control sample that is used to assess the contamination effects on accuracy due to the combined activities of sampling and analyses. Typically it is composed of analyte free matrix (e.g., deionized water) provided by the laboratory.

N. Field Sample – A portion of material received by the laboratory to be analyzed, that is contained in single or multiple containers and identified by a unique field ID number.

O. Holding Time – The elapsed time from the date/time of sample collection by the field personnel

until the date/time of its processing/analysis. Holding time requirements are dictated by the method or QAPP.

P. Homogeneity – The degree to which a property or substance is evenly distributed throughout a material.

Q. Initial Calibration – The process of analyzing standards prepared at specified concentrations, to define the quantitative response, linearity and dynamic range of the instrument to the analytes of interest. Initial calibration is performed whenever the results of a continuing calibration do not conform to the requirements of the method in use or at a frequency specified in the method.

R. Internal Standards – Analytes added to every standard, blank, lab control sample, matrix spike, matrix spike duplicate, and sample at a known concentration, prior to analysis for the purpose of adjusting the response factor used in quantitating target analytes. Internal standards are used as the basis for quantitation of the target compounds, and are generally applicable to organic analyses.

S. Laboratory Control Sample – A control sample of known composition spiked with a known concentration of analytes of interest. Aqueous and solid laboratory control samples are analyzed using the same preparation, reagents, and analytical methods employed for field samples.

T. LIMS – Laboratory Information Management System.

U. Lot – A quantity of bulk material of similar composition processed or manufactured at the same time.

V. Matrix – The predominant material of which the sample to be analyzed is composed.

W. Matrix Spike – Aliquot of sample fortified (spiked) with known quantities of specified target compounds or analytes and subjected to the entire sample preparation and analysis procedure in order to assess the appropriateness of the method for the sample matrix by measuring recovery.

X. Matrix Spike Duplicate – A second aliquot of the sample that is treated the same as the original matrix spike sample. The relative percent difference between the matrix spike and matrix spike duplicate is calculated and used to assess analytical precision.

Y. Method Blank – An analytical control consisting of a blank matrix containing all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and contamination, and to demonstrate that this level does not exceed acceptance limits. Acceptable levels of contamination are defined by project specific data quality objectives.

Z. Method Detection Limit – The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. Method

Detection Limits are determined using replicate spike samples prepared by the lab and taken through all preparation and analysis steps of the method. The method detection limit is calculated using the appropriate Student's t-parameter times the standard deviation of a series of spiked samples.

AA. Performance Audit or Evaluation – A process to evaluate the proficiency of an analyst or laboratory by evaluation of the results obtained on test materials in either a known, single or double – blind fashion.

BB. PRL – The practical reporting limit (PRL) is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operation conditions.

CC. Precision – The measurement of agreement of a set of replicate results among themselves without any prior information as to the true result. Precision is assessed by means of duplicate/replicate sample analysis.

DD. Quality Assurance – A system of policies and procedures whose purpose is to ensure, confirm and document that the product or service rendered fulfills the requirements of Pace Analytical and its client. Quality Assurance includes quality planning, quality control, quality assessment (auditing), quality reporting and corrective action.

EE. Reagent Grade – Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

FF. Replicate Samples – Samples collected at the same time, from the same place, for the same analysis, as the original sample in order to determine precision between samples.

GG. Reporting Limit (RL) – The level at which method, permit, regulatory and client specific objectives are met. The reporting limit may never be lower than the statistically determined MDL, but may be higher based on any of the above considerations. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified. Reporting limits are generally two times the MDL.

HH. Sample Delivery Group (SDG) – A unit within a single project that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a project, received over a period of up to 14 calendar days. Data from all samples in an SDG are reported concurrently. A sample Delivery Group is generally defined by one of the following, whichever occurs first:

- All samples within a project; or
- Every set of 20 field samples within a project; or
- All samples received within a 14-day calendar period

Samples may be assigned to Sample Delivery Groups by matrix (i.e., all soil samples in one

SDG, all water samples in another), at the discretion of the laboratory. Clients may establish different SDG classifications to meet project specific requirements.

KK. Sensitivity – Capability of methodology or instrumentation to discriminate between samples having differing concentrations or containing differing amounts of an analyte.

LL. Split Sample – A portion or sub-sample of a total sample obtained in such a manner that is not believed to differ significantly from other portions of the same sample.

MM. Standard – A substance or material, the properties of which are known with sufficient accuracy, to permit its use to evaluate the same property in a sample.

NN. Standard Curve – A standard curve is a curve which plots concentrations of a known analyte standard versus the instrument response to that analyte.

OO. Standard Operating Procedure –A procedure adopted for repetitive use when performing specific measurement or sampling operation. It may be an industry accepted standard method or one developed by the user.

PP. Surrogates – When employed, these are compounds added to every blank, sample, matrix spike, matrix spike duplicate, lab control sample, and standard prior to any processing or preparation; used to evaluate analytical efficiency by measuring recovery. Surrogate compounds are not expected to be detected in environmental media, but are similar to the analytes of interest. Surrogates are generally utilized for organic analyses.

VII. RESPONSIBILITIES AND DISTRIBUTION

A. Personnel

1. All personnel involved with sample preparation and analysis are responsible for adherence to this SOP. A controlled copy will be available for review and consultation within the area methods manual.

2. Personnel are responsible for ensuring that any deviations to this SOP are reported to the laboratory manager.

B. Laboratory Manager

1. The laboratory manager is responsible for ensuring adherence to this SOP and will receive a controlled copy of this SOP.

2. The laboratory manager is responsible for performing an annual review of the SOP and reporting any required revisions to the Quality Assurance Office.

C. Quality Assurance Office

1. The QA Office is responsible for conducting laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Management.

2. The QA Office is responsible for ensuring that all revisions to the SOP are implemented.

3. The QA Office is responsible for maintaining the original and complete distribution records.

D. Revisions

1. This SOP will be reviewed on an biennial basis at a minimum, and any required revisions would be incorporated.

VIII. SAMPLE COLLECTION, PRESERVATION AND HANDLING

A. SAMPLE COLLECTION

1. Sample size - One liter of water samples containing less than or equal to 1% solids should be extracted in separatory funnels. Aqueous or solid samples containing gre than 1% solids should be considered as solids and sufficient volume extracted to provide a dry weight of 10 grams (except for tissue samples and other samples noted to be reported on an as received basis). One gram aliquots are typically extracted for waste samples and samples suspected to contain high analyte levels. One hundred milligram aliquots are typically used for oil based samples, and 100 mL for milk samples.

B. SAMPLE PRESERVATION AND HANDLING

1. Collect samples in glass containers following conventional sampling practices.

2. Maintain samples at 4°C ± 2°C under darkness from the time of collection until extraction. If residual chlorine is present in aqueous samples (from chlorinated sources), add 80 mg sodium-thiosulfate per one liter of water.

3. Tissue samples are stored frozen at -18°C to -20°C under darkness.

4. All sample extracts are stored in the extract refrigerator at approximately 4°C ± 2°C until analysis.

C. HOLDING TIMES

1. Samples are typically extracted within 30 days of sample collection and the extract analyzed within 40 days of extraction. Holding times between collection and extrac or extraction and analysis do not necessarily invalidate the results. Whenever samples

are analyzed after the holding time expiration date, the results should be considered to be minimum concentrations and identified as such.

D. CRITERIA FOR ACCEPTANCE/REJECTION OF SAMPLES

1. Samples are to be rejected if information allowing determination of the applicable test and client information cannot be obtained.

2. If sample integrity has been compromised, the client must be contacted for instructions and permission to proceed with analysis. The client's comments and instructions are documented as part of routine laboratory policy.

IX. EQUIPMENT AND SUPPLIES

A. Sample bottles - 1 Liter glass amber bottles for liquids which contain less than 1% solids; 500 mL wide mouth (or smaller) glass amber bottles for solid and sludge. All bottles are purchased pre-cleaned from the vendor. If glass amber bottles are not available, samples shall be protected from the light. All bottles should have Teflon lined caps. Laboratory cleaned bottles may be substituted for pre-cleaned bottles. Bottles should be detergent washed, then solvent rinsed and baked at 450°C for one hour minimum.

B. 10 mL open top glass vials

C. 2 dram vials with Teflon-lined screw caps

D. Reacti vial - 2 mL borosilicate glass

E. 1 Liter graduated cylinder

F. Balances - 0.01g and 0.0001g

G. Drying oven

H. Soxhlet extraction apparatus

I. Thimble, 33 x 90 mm to fit Soxhlet

J. Heating mantle

K. Beakers, 50, 250, 500, 2000 Ml

L. Stainless steel spatulas

M. Assorted syringes and/or Eppendorf digital pipettes

N. Filtration apparatus

O. Glass chromatographic column – 5 ¾" disposable Pasteur pipets

P. 40 mL vial with caps

Q. 60 mL vial with caps with septa

R. Glass wool pre-extracted with methylene chloride dried, and stored in a clean air tight plastic bag

S. Glass funnel, 125-250 mL

T. Glass fiber filter paper (Whatman GF/D or equivalent)

U. Centrifuge apparatus - capable of rotating 500 mL centrifuge bottles or 15 mL tubes at 5000 rpm minimum

V. Disposable Pasteur pipettes

W. Disposable serological 10 mL pipettes

X. 500 mL Kuderna Danish (KD) concentrator apparatus

Y. Teflon boiling chips – pre-rinsed with methylene chloride

Z. Water bath, ultrasonic

AA. Desiccator

BB. Nitrogen evaporation system with variable flow rate

CC. Volumetric flasks - 5 mL, 10 mL, 15 mL, 20 mL, 25 mL and 100 mL

DD. Teflon tape

EE. Low volume autosampler vial with crimp caps

FF. Sodium hydroxide - reagent grade. Dissolve 40 g NaOH in 1L reagent water.

GG. Potassium Phosphate – reagent grade – Dissolve 68.05 g KH_2PO_4 in 1 L reagent H_20

HH. Sulfuric acid - reagent grade (sp gravity 1.84)

II. Silica gel – chromatographic grade, 60-100 mesh

JJ. Celite – reagent grade

KK. Anhydrous sodium sulfate - Rinse with methylene chloride (20 mL/g) and bake at 130°C for 1 hour minimum. Store baked anhydrous sodium sulfate in oven until use. Cool prior to use.

LL. 100-400 mesh carbon/Celite mixture

MM. Solvents - Acetone, toluene, hexane, cyclohexane, nonane, methanol and methylene chloride. All solvents must be distilled in glass and pesticide grade.

NN. Alumina – activity grade

OO. White quartz sand 60/70 mesh

PP. Diatomeous earth

QQ. Reference matrices

1. Reagent water

2. Playground sand or similar material which is free of target compounds; may be prepared by extraction with methylene chloride and/or baking at 450°C for 4 hours.

3. Fish tissue, pre-tested to be analyte free

4. Filter paper - Gelman type A or equivalent

5. Mineral Oil

6. Milk, whole

RR. Individual standards prepared as described in the "Procedure" section of this SOP.

X. REAGENTS AND STANDARDS

A. Standards and working solutions are prepared from or compared to certified standards or purchased as certified premixed standards. All standards are valid for 1 year from date opened (or prepared). All standards are stored in glass bottles and stored at 4°C ± 2°C. Standards may be re-verified by comparison to a valid native analyte solution. The final concentrations determined for any solution being re-verified must be within 20% of the expected concentrations for that solution.

B. The preparation of standards and working solutions is thoroughly documented in the appropriate standards notebook. Such documentation allows the traceability of each solution to

a certified, purchased solution.

C. Preparation of Primary Stock Solution of Internal Standards (AI2-#)

Note: Identification AI2-# - # denotes the next sequential number assigned to AI2 standard from the Dioxin Standard Notebook.

Compound	If Concentration is µg/mL	Amount Added (µL)	Final Concentration (µg/mL)
2,3,7,8-TCDD-$^{13}C_{12}$	50	200	2.08
2,3,7,8-TCDF-$^{13}C_{12}$	50	200	2.08
1,2,3,7,8-PeCDD-$^{13}C_{12}$	50	200	2.08
1,2,3,7,8-PeCDF-$^{13}C_{12}$	50	200	2.08
2,3,4,7,8-PeCDF-$^{13}C_{12}$	50	200	2.08
1,2,3,4,7,8-HxCDD-$^{13}C_{12}$	50	200	2.08
1,2,3,6,7,8-HxCDD-$^{13}C_{12}$	50	200	2.08
1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	50	200	2.08
1,2,3,6,7,8-HxCDF-$^{13}C_{12}$	50	200	2.08
1,2,3,7,8,9-HxCDF-$^{13}C_{12}$	50	200	2.08
2,3,4,6,7,8-HxCDF-$^{13}C_{12}$	50	200	2.08
1,2,3,4,6,7,8-HpCDD-$^{13}C_{12}$	50	200	2.08
1,2,3,4,6,7,8-HpCDF-$^{13}C_{12}$	50	200	2.08
1,2,3,4,7,8,9-HpCDF-$^{13}C_{12}$	50	200	2.08
OCDD-$^{13}C_{12}$	10	2000	4.17

1. All compounds should be purchased in nonane (Cambridge or equivalent).

Note: Stock solutions containing labeled PCDDs (DS-1000) and PCDFs (FS-1000) at concentrations of 1.0 ng/uL (2.0 ng/uL for OCDD-$^{13}C_{12}$) are also available from Wellington Laboratories. Equal amounts of these solutions may be combined and diluted 10x total to prepare the BI2 secondary solution described below.

2. Sonicate each vial for at least 1 minute after bringing to room temperature.

3. After sonication, pipette the compounds noted above into a pre-rinsed 2 dram vial and label. Identification should include: ID# and log #, $^{13}C_{12}$ primary stock solution of internal standard, preparation date, expiration date and preparer's initials.

4. Mark the meniscus now and each time a portion is removed.

5. Seal vial with Teflon tape and store in standards freezer at <0°C.

6. Record all standard preparation information in Dioxin Standard Notebook.

D. Preparation of Internal Standard Secondary Stock (BI2-#)

1. Sonicate the primary stock (AI2-#) for five minutes and allow it to reach room temperature before using.

2. Using an Eppendorf pipette, add 481 µL of primary stock (AI2-#) into a pre-rinsed 10 mL volumetric flask and bring to volume with tridecane to prepare the 100 ng/mL (200 ng/mL OCDD-$^{13}C_{12}$) solution. Alternately, combine the purchased Wellington stock solutions (1 mL each) and bring to 10 mL with tridecane to prepare the 100 ng/mL (200 ng/mL OCDD-$^{13}C_{12}$) solution.

3. Sonicate for five minutes and transfer into clean labeled vials. Identification should include: ID#, (BI2-#), log #, vial numbers, preparation date and preparer's initials.

   Note: Identification BI2-# - # denotes the next sequential number assigned to BI2 standard from the Dioxin Standard Notebook.

4. Seal with Teflon tape, mark the meniscus (now and after each use) and store in the standards refrigerator.

5. Record all standard preparation information in Dioxin Standard Notebook.

6. This solution may otherwise be purchased as a prepared mix from Wellington Laboratories or equivalent.

E. Preparation of Internal Standard Spiking Solution (CI2-#)

1. Sonicate secondary standard (BI2-#) for five minutes and allow it to reach room temperature before using.

2. Add 20 µL of BI2-# per mL in appropriate pre-rinsed volumetric flask and bring to volume with acetone to prepare this 2 ng/mL solution. Prepare only enough spiking solution as will be used in one day.

3. Sonicate for five minutes.

4. Transfer spiking solution into a pre-rinsed 6 dram vial labeled with ID# (CI2-#), log #, preparation date, expiration date and preparer's initials.

   Note: Identification CI2-# - # denotes the next sequential number assigned to the CI2 standard from the Dioxin Standard Notebook.

5. Prior to extraction, one mL of this solution is added to each sample.

F. Preparation of Primary Native Standard Spiking Solution (AN1-#)

Compound	Concentration (µg/mL)
2,3,7,8-TCDF	0.40
2,3,7,8-TCDD	0.40
1,2,3,7,8-PeCDD	2.0
1,2,3,7,8-PeCDF	2.0
2,3,4,7,8-PeCDF	2.0
1,2,3,4,7,8-HxCDD	2.0
1,2,3,6,7,8-HxCDD	2.0
1,2,3,7,8,9-HxCDD	2.0
1,2,3,4,7,8-HxCDF	2.0
1,2,3,6,7,8-HxCDF	2.0
1,2,3,7,8,9-HxCDF	2.0
2,3,4,6,7,8-HxCDF	2.0
1,2,3,4,6,7,8-HpCDD	2.0
1,2,3,4,6,7,8-HpCDF	2.0
1,2,3,4,7,8,9-HpCDF	2.0
OCDF	4.0
OCDD	4.0

1. This is a purchased solution in nonane (Cambridge, TerraChem, or equivalent).

   NOTE: One vendor source and standards prepared from the source are used for the ICAL. The other vendor source and standards diluted from it are used as an independent validation of all standards purchased.

2. Divide the standard into pre-rinsed 1 mL vials with ID# (AN1-#), log #, Primary Native Spiking Solution. Identification should also include: preparation date, expiration date and preparer's initials.

   Note: Identification AN1-# - # denotes the next sequential number assigned to AN1 standard from the Dioxin Standard Notebook.

3. Mark the meniscus now and after each use.

4. Seal with Teflon tape and store in standards refrigerator at 4°C ± 2°C.

5. Record all standard preparation information in Dioxin Standard Notebook.

G. Preparation of Native Secondary Stock (BN1-#)

1. Sonicate primary standard (AN1-#) for five minutes and allow it to reach room

temperature before using.

2. Add 1.0 mL of AN1-# to a pre-rinsed 10 mL volumetric flask and bring to volume with tridecane to prepare this 40 ng/mL solution.

3. Sonicate for five minutes after preparation and transfer into 2 dram vials. Identification should include: Native Spiking Solution ID# (BN1-#), log #, preparation date, expiration date and preparer's initials.

   Note: Identification BN1-# - # denotes the next sequential number assigned to BN1 standard from the Dioxin Standard Notebook.

4. Seal vials with Teflon tape, mark the meniscus (now and after each use), and store in the standards refrigerator at 4°C ± 2°C until ready to use.

5. Record all standard preparation information in Dioxin Standard Notebook.

H. Preparation of Native Spiking Solution (CN1-#)

1. Sonicate secondary standard (BN1-#) for five minutes and allow it to reach room temperature before using.

2. Add 10 µL of BN1-# to a pre-rinsed 2 dram vial and 1990 µL of acetone to prepare this 200 pg/mL solution.

3. Sonicate for five minutes.

4. Label 2 dram vial with ID# (CN1-#), log #, preparation date, expiration date and preparer's initials.

   Note: Identification CN1-# - # denotes the next sequential number assigned to CN1 standard from the Dioxin Standard Notebook.

5. Record all standard preparation information in Dioxin Standard Notebook.

6. Prior to extraction, one mL of this solution is added to each laboratory and matrix spike sample.

I. Preparation of Cleanup Standard Primary Stock (ACl4-#)

Compound	If Concentration is µg/mL	Amount Added (µL)	Final Concentration (µg/mL)
$^{37}Cl_4$ 2,3,7,8-TCDD	50	200	1.0

1. The 50 µg/mL solution is purchased in nonane (Cambridge or equivalent). Sonicate the solution for five minutes and allow to reach room temperature and add 200 µL of the solution to a pre-rinsed 10 mL volumetric flask and bring to volume with tridecane to prepare this 1 ug/mL solution.

2. Transfer the standard to a 2 dram vial with color coded tape. Identification should include: $^{37}Cl_4$ Cleanup Standard: Primary Stock ID# (ACl4-#), log #, preparation date, expiration date and preparer's initials.

   Note: Identification ACl4-# - # denotes the next sequential number assigned to ACl4 standard from the Dioxin Standard Notebook.

3. Seal vials with Teflon tape, mark the meniscus (now and after each use), and store in the standards refrigerator at 4°C ± 2°C.

4. Record all standards preparation information in Dioxin Standard Notebook.

J. Preparation of $^{37}Cl_4$ Cleanup Standard Secondary Stock (BCl4-#)

1. Sonicate the Cleanup Standard Primary Stock (CSPS) for five minutes and allow it to reach room temperature.

2. Using an Eppendorf pipette, add 1 mL of CSPS (ACl4-#) into a pre-rinsed 25 mL volumetric flask. Bring to volume with tridecane to prepare this 40 ng/mL solution.

3. Sonicate for five minutes, transfer to 2 dram vials. Identification should include: ID# (BCl4-#), log #, vial numbers, preparation date, expiration date and preparer's initials.

   Note: Identification BCl4-# - # denotes the next sequential number assigned to BCl4 standard from the Dioxin Standard Notebook.

4. Seal vials with Teflon tape, mark the meniscus (now and after each use), and store in standards refrigerator at 4°C ± 2°C.

5. Record all standard preparation information in Dioxin Standard Notebook.

K. Preparation of $^{37}Cl_4$ Cleanup Standard Spiking Solution (CCl4-#)

1. Sonicate the compound (BCl4-#) for five minutes and allow it to reach room temperature.

2. Using an Eppendorf pipette, add 2 mL of BCl4-# into a pre-rinsed 100 mL volumetric flask and bring to volume with tridecane to prepare this 800 pg/mL.

3. Sonicate for five minutes and transfer to pre-rinsed 6 dram vials. Identification should

include ID# (CCl4-#), log #, vial number, preparation date, expiration date and preparer's initials.

Note: Identification CCl4-# - # denotes the next sequential number assigned to CCl4 standard from the Dioxin Standard Notebook.

4. Seal vials tightly with Teflon tape, mark the meniscus (now and after each use), and store in standards refrigerator at 4°C ± 2°C.

5. Record all standard preparation information in Dioxin Standard Notebook.

6. 250 µL of this solution is added to each sample between extraction and enrichment.

L. Preparation of $^{13}C_{12}$ Recovery Standard Primary Stock (AR2-#)

Compound	If Concentration is µg/mL	Amount Added (µL)	Final Concentration (µg/mL)
1,2,3,4-TCDD-$^{13}C_{12}$	50	250	2.5
1,2,3,7,8,9-HxCDD-$^{13}C_{12}$	50	250	2.5

1. The individual 50 µg/mL solutions are purchased in nonane (Cambridge or equivalent). Sonicate the solutions for five minutes and allow to reach room temperature.

2. Add the listed amount of each standard to a pre-rinsed 5 mL volumetric flask and bring to volume with tridecane.

3. Transfer the standard to a labeled 2 dram vials. Identification should include: ID# (AR2-#), log #, $^{13}C_{12}$ Recovery Standard, number of vials, preparation date, expiration date and preparer's initials.

   Note: Identification AR2-# - # denotes the next sequential number assigned to AR2 standard from the Dioxin Standard Notebook.

4. Seal vials with Teflon tape, mark the meniscus (now and after each use), and store in the standards refrigerator at 4°C ± 2°C.

5. Record all standard preparation information in Dioxin Standard Notebook.

M. Preparation of $^{13}C_{12}$ Recovery Standard Spiking Solution (CR3-#)

1. Sonicate the $^{13}C_{12}$ Primary Recovery Standard for five minutes and allow it to reach room temperature before using.

2. Using an Eppendorf pipette, add 2 mL of AR2-# into a pre-rinsed 25 mL volumetric

flask. Bring to volume with tridecane to prepare this 200 ng/mL solution.

3. Sonicate for five minutes, transfer to 2 dram vials labeled with tape. Identification should include: ID# (CR3-#), log #, vial numbers, preparation date, expiration date and preparer's initials.

   Note: Identification CR3-# - # denotes the next sequential number assigned to CR3 standard from the Dioxin Standard Notebook.

4. Seal vials with Teflon tape, mark the meniscus (now and after each use), and store in standards refrigerator at 4°C ± 2°C.

5. Record all standard preparation information in Dioxin Standard Notebook.

6. 10 µL of this solution is added to each sample during the final concentration of the extract.

7. This solution may otherwise be purchased as a prepared mix from Wellington Laboratories or equivalent.

N. Preparation of Initial Calibration Solutions

1. Mix 256 µL of AN1-# with 100 µL of ACl4-#. Label as ICAL Native Mix. This solution contains 281 pg/µL of the native and $^{37}Cl_4$ labeled isomers.

2. Prepare a 1:50 dilution (20 µL to 1 mL) of the ICAL Native Mix and label as Diluted ICAL Native Mix. This solution contains the native and $^{37}Cl_4$ labeled isomers at 5.6 pg/µL.

3. Mix 150 µL of AI2-# with 125 µL of AR2-#. Label as ICAL Internal Mix. This solution contains the internal and recovery standards at 1.13 ng/µL.

4. Prepare the five calibration solutions as follows:

CS-1	22.2 µL	Diluted ICAL Native
fv = 250 µL	22 µL	ICAL Internal Mix
	206 µL	Tridecane
CS-2	89 µL	Diluted ICAL Native Mix
fv = 250 µL	22 µL	ICAL Internal Mix
	139 µL	Tridecane
CS-3	35.6 µL	ICAL Native Mix
fv = 1 mL	88 µL	ICAL Internal Mix
	876 µL	Tridecane
CS-4	35.6 µL	ICAL Native Mix
fv = 250 µL	22 µL	ICAL Internal Mix
	192 µL	Tridecane
CS-5	178 µL	ICAL Native Mix
fv = 250 µL	22 µL	ICAL Internal Mix
	50 µL	Tridecane

Note: These solutions contain the standards at the concentration levels described on the Table found on the next page. Split CS-3 aliquot into three separate vials. Archive two vials in the standards refrigerator.

PCDD/PCDF	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,7,8,9-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100
$^{13}C_{12}$-OCDD	100	100	100	100	100
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

The calibration solutions may otherwise be purchased as a prepared mix from Wellington Laboratories or equivalent. The CS-3 is also available with the window defining and column resolution isomers in the sar. solution (See Quality Control Section).

XI. CALIBRATION

A. Initial Calibration

1. Prior to analyzing samples, the instrument is calibrated by analyzing a series of five standard solutions. This initial calibration (ICAL) is performed when the continuing calibration solution is replaced by one from a different lot or when the continuing calibration does not pass the method specified criteria (Section 7.7.4, Method 8290; ±20% natives and ±30% internal standards). A signal to noise ratio of >5:1 is required for each isomer.

2. Additional standards are analyzed to demonstrate chromatographic resolution and stability of the ICAL. These consist of the continuing calibration solution described above, and a purchased solution (Wellington 5TDWD or equivalent) containing the isomers required to demonstrate the chromatographic resolution of the 2,3,7,8-TCDD (25% valley) and the presence of the first and last eluting isomers of each congener class. A solution (Wellington EPA-1613-CS3WT) is available and incorporates all of the above components into a single solution.

B. Calibration Standards Acceptance Criteria

1. Standards must meet the following requirements before analyzing samples.

a) Ratios must be within 15% of theoretical values. Any outliners are flagged in AutoPro.

b) Initial calibration relative standard deviations must be less than 20% for the native isomers and 30% for the labeled isomers.

c) Continuing calibration standards are analyzed at the beginning and end of each day and must yield response factors within 20% (natives) to 30% (labeled) of the initial calibration.

d) Percent valley between 2,3,7,8-TCDD and any other peak in the column performance check must be <25%, relative to the height of 2,3,7,8-TCDD.

e) All peaks for a given PCDD/PCDF level of chlorination must elute within the window(s) set up for that particular class (determined from the window defining mix which contains first and last eluting isomers).

f) Native compounds must elute within ±2 seconds of the expected elution time relative to the elution times of the corresponding internal standards.

XII. PROCEDURE

A. Glassware Cleaning

1. Prior to use, glassware should be cleaned using the following steps:

   a) Wash with soap and water (water rinse).

   b) Soak in Chemsolve (or equivalent) for one hour (water rinse). Note: Chemsolve should be changed on a weekly basis at minimum, or after washing of samples found to contain very high analyte levels.

   c) Rinse with tapwater.

   d) Rinse with 1 N nitric acid and then a DI rinse

   e) Rinse with methanol and then acetone.

   f) Air Dry. Rinse with hexane and the solvent to be used for extraction just prior to glassware use.

Note: The brushes should be replaced on a weekly basis at minimum, or after glassware used for samples containing very high analyte levels, in order to minimize the chances for contamination during the cleaning process.

B. PREPARATION PRIOR TO SAMPLE EXTRACTION

1. Aqueous samples containing one percent solids (or less) are extracted in separatory funnels.

2. In samples expected or known to contain high levels of the PCDDs and /or PCDFs, the smallest sample size representative of the entire sample should be used, and the extract should be diluted, if necessary.

3. Determination of Percent Solids

   a) Weigh 5-10 g of sample to three significant figures into a tarred weighing vessel.

   b) Dry overnight (minimum of 12 hours) at 110 ± 5°C and cool in a desiccator. Reweigh.

   c) % Solids = $\frac{\text{Wt dried sample (g)} \times 100}{\text{Wt wet sample(g)}}$

d) Data are recorded electronically and printed out as needed.

4. Soxhlet/Dean Stark Glassware Pre-extraction

a) Place 30-40 mL of toluene in the extractor and 200-250 mL in the flask along with approximately 5-8 Teflon boiling chips.

b) Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1-2 drops of toluene per second will fall from the condenser tip into the receiver. Extract the apparatus for 3-4 hours minimum (typically overnight).

c) After pre-extraction, disassemble the apparatus. Concentrate and collect the solvent rinse. The solvent rinse may be archived for troubleshooting purposes.

5. Aqueous Sample Preparation (<1% Solids)

a) Mark the original level of the sample on the sample bottle for later determination of sample volume. Weigh the sample in the bottle to ± 1 g on a top loading balance. Record this weight.

b) Spike 1 mL of the labeled compound solution (CI2-#) into the bottle. Cap the bottle and mix by carefully shaking for 2 minutes.

c) For each sample or sample set (up to 10) to be extracted during the same eight hour shift, place two 1.0 L aliquots of reagent water in clean 1 L Erlenmeyer flasks. If larger batches (up to 20) are to be extracted, include one additional aliquot of reagent water. Only one LCS is required when MS/MSDs are also prepared in the sample batch.

d) A matrix spike and matrix spike duplicate are typically extracted along with the sample set (up to 20) extracted. Place the two 1.0 L aliquots of client-supplied duplicate water samples in clean 1 L Erlenmeyer flasks.

e) Spike 1 mL of the labeled compound solution (Cl2-#) into one reagent water. This aliquot will serve as the blank. Spike 1 mL of labeled compound solution (Cl2-#) and 1 mL of the native spiking solution (CN1-#) into the remaining reagent water aliquot(s). This (they) will serve as the laboratory control spike(s). Spike 1 mL of labeled compound solution (Cl2-#) and 1 mL of the native spiking solution (CN1-#) into the client-supplied duplicate water samples (if supplied). These samples will serve as the matrix spike/spike duplicate samples.

Note: When setting up method blanks, the glassware set used shall be varied randomly amongst the sets used for sample extraction.

f) Assemble a Buchner funnel and a vacuum adapter on top of a clean 1 L Erlenmeyer flask. Apply a vacuum to the flask and pour the entire contents of the sample bottle through a glass fiber filter in the Buchner funnel, swirling the sample remaining in the bottle to suspend any particulate. Rinse the bottles with three 60 mL portions of methylene chloride, pouring each portion through the filter. Samples containing no particulate need not be filtered; instead, quantitatively transfer the samples to separatory funnels. Treat the QC samples in the same manner as the field samples.

g) If filtered, rinse any particulate off the sides of the Buchner funnel with small quantities of methylene chloride.

h) Weigh the empty sample bottle on a top loading balance to ± 1 g. Determine the weight of the sample by difference and note the weight on the extraction preparation sheet. This value is used in the calculation of analyte concentrations.

i) Save and extract the filter, particulate and filtrates as described below.

6. Preparation of Aqueous Samples containing >1% solids

a) Weigh a well mixed aliquot of each sample sufficient to provide 10 g of dry solids (based on the solids determination described above) into a clean beaker, pre-extracted thimble or glass jar. In certain cases, i.e., sludge or waste matrices, this amount may be modified to a smaller aliquot to provide more workable extracts.

b) Spike with 1 mL of the labeled compound solution (CI2-#).

c) For each sample or sample set (up to 10) to be extracted in the same eight hour shift, weigh two 10 g aliquots of clean sand and place each aliquot into a Soxhlet thimble. If larger batches (up to 20) are to be extracted, include an additional aliquot of reference matrix material. (Sand is pre-extracted prior to use.)

d) A matrix spike and matrix spike duplicate are typically extracted along with the sample set (up to 20) extracted. Place the appropriate weight of client-supplied duplicate samples into clean beakers or glass jars. If an MS/MSD is prepared with the sample batch, only one lab spike is required.

e) Spike one reference sample with 1 mL of the labeled spiking solution (CI2-#). This aliquot will serve as the method blank.

Note: When setting up method blanks, the glassware set used shall be varied randomly amongst the sets used for sample extraction.

f) Spike the other aliquot(s) with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). This (they) will serve as the laboratory control spike(s).

g) Spike the client-supplied duplicate samples with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). These samples will serve as the matrix spike/matrix spike duplicate set (if required).

h) If sample flows easily, assemble a Buchner funnel and a vacuum adapter on top of a clean 1 L Erlenmeyer flask. Apply a vacuum to the flask and pour the aliquot through a glass fiber filter in the Buchner funnel, swirling the sample remaining in the bottle to suspend any particulate. Rinse the bottle 3 times with 60 mL of reagent water pouring each aliquot through the filter.

i) If filtered, rinse any particulate off the sides of the Buchner funnel with small quantities of methylene chloride.

j) Save and extract the filtrates as described below. (If greater than 50 mL of water is present, extract it in a separatory funnel and combine with the solid extract, otherwise discard aqueous phase.)

7. Preparation of Multiphase Samples

a) Spike an appropriately sized aliquot of the sample with 1 mL of the labeled compound solution (CI2-#).

b) For each sample or sample set (up to 10) to be extracted in the same eight hour shift, weigh two 10 g aliquots of clean sand and place each aliquot into a Soxhlet thimble. If larger batches (up to 20) are to be extracted, include an additional aliquot of reference matrix material. (Sand is pre-extracted prior to use.)

c) A matrix spike and matrix spike duplicate are typically extracted along with the sample set (up to 20) extracted. Place the appropriate weight of client-supplied duplicate samples into clean beakers or glass jars. If an MS/MSD is prepared with the sample batch, only one lab spike is required.

d) Spike one reference sample with 1 mL of the labeled compound solution (CI2-#). This aliquot will serve as the method blank.

Note: When setting up method blanks, the glassware set used shall be varied randomly amongst the sets used for sample extraction.

e) Spike the other aliquot(s) with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). This (they) will serve as the

laboratory control spike(s).

f) Spike the client-supplied duplicate samples with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). These samples will serve as the matrix spike/matrix spike duplicate set (if required).

g) Pressure filter the sample, blank and laboratory control spike aliquots through Whatman GF/D glass fiber filter paper. If necessary, centrifuge these aliquots for 30 minutes prior to filtration.

h) Discard aqueous phase. (If aqueous phase is 50 mL or greater, a separatory funnel extraction is performed and the extract is combined with the extract form the solid portion.) Remove any non-aqueous liquid (if present) and reserve for recombination with the extract of the solid phase. Prepare the filter papers of the sample and QC aliquots for particle size reduction and blending.

i) Prior to spiking, samples with particle size greater than 1 mm are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix dependent.

j) In general, hard particles can be reduced by grinding with a mortar and pest' Softer particles can be reduced by grinding in a Wiley mill or meat grinder, homogenization, or by blending.

k) The grinding, homogenization, or blending procedures should be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

l) Tissue samples, certain papers and pulps, slurries and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process.

8. Preparation of Solid Samples by ASE

a) If the client requests that results be reported on a dry weight basis, a separate amount of sample will be weighed, dried overnight in an oven, and the percent solids calculated. This is recorded on the dry weight sheet used in reporting results

b) Attach and tighten bottom cap onto ASE extraction cell, and insert cellulose extraction filter. Seat filter firmly into bottom of tube. If sample appears wet add about 10-25 g of sodium sulfate to cell. Weigh out 10 g dry weight of sample aliquot into extraction cell. If the sample appears oily, check with th client to confirm using a smaller sample size of 1-3 grams.

c) Spike the sample aliquot with the labeled spiking solution (CI2-#).

d) For each sample or sample set (up to 10) to be extracted in the same eight hour shift, weigh two 10 g aliquots of clean sand and place each aliquot into an extraction vessel. If larger batches (up to 20) are to be extracted, include an additional aliquot of reference matrix material. (Sand is pre-extracted prior to use.)

e) A matrix spike and matrix spike duplicate are typically extracted along with the sample set (up to 20) extracted. Place the appropriate weight of client-supplied duplicate samples into clean beakers or glass jars. If an MS/MSD are prepared, only one lab spike is required.

f) Spike one reference sample with 1 mL of the labeled compound solution (CI2-#). This aliquot will serve as the method blank.

Note: When setting up method blanks, the extraction vessel used shall be varied randomly amongst the sets used for sample extraction.

g) Spike the other aliquot(s) with 1 mL of the labeled spiking solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). This (they) will serve as the laboratory control spike(s).

h) Spike the client-supplied duplicate samples with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). These samples will serve as the matrix spike/matrix spike duplicate set (if required).

i) Place loaded ASE cells into slots in the top tray of the ASE. Place labeled 60 mL vials with septa caps into the corresponding slots in the bottom tray. UNLOCK TRAYS AND TURN NITROGEN SUPPLY ON BEFORE ATTEMPTING TO MOVE TRAYS! Only label the vials in the area shown on the diagram in the ASE operator's manual.

j) Verify that the rinse vials are not full, the solvent waste vial is not full, and the solvent reservoir has sufficient solvent mixture for the sample set that is to be run. Check that there is sufficient Nitrogen pressure for the entire run, also. Load the correct method into the ASE, and run a few rinse cycles to ensure a clean system. Press the start button to begin the run.

k) After the ASE has completed the sample extractions, unlock the trays and remove the vials for spiking with surrogate and clean-up steps. Remove the cells and disassemble them. CELLS WILL BE VERY HOT WHEN THEY COME OUT OF THE OVEN! Send the tubes and caps to the dish room for cleaning, and sonicate the frits, PEEK seals, thread inserts, and snap rings in

toluene. Re-assemble cells when parts are cleaned and rinsed and store with the caps on the tubes to prevent thread damage.

9. Preparation of Soil/Solid Samples by Soxhlet

a) Weigh a 10 gram aliquot (dry weight) of the homogenized sample, place into a Soxhlet thimble and cover with glass wool and sand. If the sample material is wet, dry it by mixing with extracted anhydrous sodium sulfate until free flowing before adding to the Soxhlet thimble. Mix sample and sand well. If the sample will be extracted using Soxhlet Dean-Stark apparatus (with toluene), no sodium sulfate should be added.

b) Spike the sample aliquot with the labeled spiking solution (CI2-#).

c) For each sample or sample set (up to 10) to be extracted in the same eight hour shift, weigh two 10 g aliquots of clean sand and place each aliquot into a Soxhlet thimble. If larger batches (up to 20) are to be extracted, include an additional aliquot of reference matrix material. (Sand is pre-extracted prior to use.)

d) A matrix spike and matrix spike duplicate are typically extracted along with the sample set (up to 20) extracted. Place the appropriate weight of client-supr duplicate samples into clean beakers or glass jars. If an MS/MSD is prepar with the sample batch, only one lab spike is required.

e) Spike one reference sample with 1 mL of the labeled compound solution (CI2-#). This aliquot will serve as the method blank.

Note: When setting up method blanks, the glassware set used shall be varied randomly amongst the sets used for sample extraction.

f) Spike the other aliquot(s) with 1 mL of the labeled spiking solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). This (they) will serve as the laboratory control spike(s).

g) Spike the client-supplied duplicate samples with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). These samples will serve as the matrix spike/matrix spike duplicate set (if required).

h) Prior to spiking, samples with particle size greater than 1 mm are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix dependent.

i) In general, hard particles can be reduced by grinding with a mortar and pest Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by

homogenization, or by blending.

j) The grinding, homogenization, or blending procedures should be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

k) Tissue samples, certain papers and pulps, slurries and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process.

10. Preparation and Extraction of Still Bottom Samples

a) Transfer a 1.0 g ±0.05 g aliquot of the homogenized sample to a clean 50 mL beaker and spike the sample with 1 mL of the labeled spiking solution (CI2-#).

b) For each sample or sample set (up to 10) to be extracted in the same eight hour shift, weigh two 1 g aliquots of clean sand and place each aliquot into a Soxhlet thimble. If larger batches (up to 20) are to be extracted, include an additional aliquot of reference matrix material. (Sand is pre-extracted prior to use.)

c) A matrix spike and matrix spike duplicate are typically extracted along with the sample set (up to 20) extracted. Place the appropriate weight of client-supplied duplicate samples into clean beakers or glass jars. If an MS/MSD is prepared with the sample batch, only one lab spike is required.

d) Spike one reference material aliquot with 1 mL of the labeled compound solution (CI2-#). This aliquot will serve as the method blank.

Note: When setting up method blanks, the glassware set used shall be varied randomly amongst the sets used for sample extraction.

e) Spike the other aliquot(s) with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). This (they) will serve as the laboratory control spike(s).

f) Spike the client-supplied duplicate samples with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). These samples will serve as the matrix spike/matrix spike duplicate set (if required).

g) Add 10 mL of toluene to the beaker and mix well.

h) Filter the solution through a pre-rinsed glass fiber filter into a 50 mL round bottom flask. Rinse the beaker and filter with three 10 mL aliquots of toluene.

i) Concentrate the extracts and rinsates to NEAR dryness on a rotary evaporator at 50°C, a K-D flask, or under a gentle stream of nitrogen.

11. Preparation of Fly Ash Samples

a) Weigh a 10g aliquot of the homogenized sample and an equivalent amount of anhydrous sodium sulfate into a clean beaker. Mix well. Note: If high levels are expected, a smaller (1 gram) aliquot may be extracted. If the sample will be extracted using Soxhlet Dean-Stark apparatus (with toluene), no sodium sulfate should be added.

b) Spike the sample aliquot with 1 mL of the labeled compound solution (CI2-#).

c) For each sample or sample set (up to 10) to be extracted in the same eight hour shift, weigh two 10 g aliquots of clean sand and place each aliquot into a Soxhlet thimble. If larger batches (up to 20) are to be extracted, include an additional aliquot of reference matrix material. (Sand is pre-extracted prior to use.)

d) A matrix spike and matrix spike duplicate are typically extracted along with the sample set (up to 20) extracted. Place the appropriate weight of client-supplied duplicate samples into clean beakers or glass jars. If an MS/MSD is prepare with the sample batch, only one lab spike is required.

e) Spike one aliquot of the reference matrix material with 1 mL of the labeled compound solution (CI2-#). This aliquot will serve as the method blank.

Note: When setting up method blanks, the glassware set used shall be varied randomly amongst the sets used for sample extraction.

f) Spike the other aliquot(s) with 1 mL of the labeled spiking solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). This (they) will serve as the laboratory control spike(s).

g) Spike the client-supplied duplicate samples with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). These samples will serve as the matrix spike/matrix spike duplicate set (if required).

12. Preparation of Milk and Milk Product Samples

a) Accurately measure a 100 mL aliquot of milk and transfer to a 2 liter separatory funnel.

b) Spike the sample aliquot with 1 mL of the labeled compound solution (CI2-#

c) For each sample or sample set (up to 10) to be extracted in the same eight hour

shift, measure two 100 mL aliquots of de-ionized water into clean separatory funnels. If larger batches (up to 20) are to be extracted, include an additional aliquot of the reference matrix material.

d) A matrix spike and matrix spike duplicate will be extracted along with the sample set (up to 20). Place the appropriate weight of client-supplied duplicate samples into 2 Liter separatory funnels.

e) Spike one reference matrix material with 1 mL of the labeled compound solution (CI2-#). This aliquot will serve as the method blank.

Note: When setting up method blanks, the glassware set used shall be varied randomly amongst the sets used for sample extraction.

f) Spike the other aliquot(s) with 1 mL of the labeled spiking solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). This (they) will serve as the laboratory control spike(s).

g) Spike the client-supplied duplicate samples with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). These samples will serve as the matrix spike/matrix spike duplicate set (if required).

13. Preparation of Tissue Samples

a) If the sample is supplied as whole fish or fillets, grind the sample using a meat grinder or blender.

b) Weigh a 10 gram aliquot of the homogenized sample into a clean beaker. Mix in enough extracted anhydrous sodium sulfate to dry the sample (usually approximately 20 grams). If the sample will be extracted using Soxhlet Dean-Stark apparatus (with toluene), no sodium sulfate should be added.

c) Quantitatively transfer the sample into a clean Soxhlet thimble and top with extracted glass wool.

d) Spike the sample aliquot with the labeled spiking solution (CI2-#).

e) For each sample or sample set (up to 10) to be extracted in the same eight hour shift, weigh two 10 g aliquots of clean fish and place each aliquot into a Soxhlet thimble. If larger batches (up to 20) are to be extracted, include an additional aliquot of reference matrix material. If an MS/MSD are run with the extraction batch, only one LCS is required.

f) A matrix spike and matrix spike duplicate will be extracted along with the sample set (up to 20). Place the appropriate weight of client-supplied duplicate

samples into Soxhlet thimbles

g) Spike one reference sample with 1 mL of the labeled compound solution (CI2-#). This aliquot will serve as the method blank.

Note: When setting up method blanks, the glassware set used shall be varied randomly amongst the sets used for sample extraction.

h) Spike the other aliquot(s) with 1 mL of the labeled spiking solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). This (they) will serve as the laboratory control spike(s).

i) Spike the client-supplied duplicate samples with 1 mL of the labeled compound solution (CI2-#) and 1 mL of the native spiking solution (CN1-#). These samples will serve as the matrix spike/matrix spike duplicate set (if required).

j) Store any remaining sample in the freezer at approximately -18°C.

k) If the sample will be extracted using Soxhlet Dean-Stark apparatus (with toluene), no sodium sulfate should be added.

C. SAMPLE EXTRACTION

1. Filtrates

a) Quantitatively transfer the filtrate into a separatory funnel with three 35 mL rinses of $MeCl_2$.

b) Extract by shaking the separatory funnel, venting any back pressure.

c) If an emulsion layer forms, allow it to dissipate, or use mechanical or chemical (salt, heat ,etc.) means to break the emulsion. Once the emulsion is broken, continue the extraction.

d) After the extraction allow the layers to separate.

e) Remove the methylene chloride layer. Repeat the extraction two times with fresh aliquots of methylene chloride, combining the three solvent portions.

f) Transfer the methylene chloride through a 10 cm plug of sodium sulfate and glass wool to a pre-extracted Kuderna Danish concentrator. Set aside for addition of filter and particulate extract (if applicable) or concentrate to approximately 1 mL using KD and N-evap apparatus and proceed with samp' cleanup.

2. Sludge or Samples with >1% solids

a) Load the wet sample aliquot into the thimble and mix with enough anhydrous sodium sulfate to dry the sample. Use a similar approach for the filter and particulate sample from a filtered sample aliquot. Alternatively, the extraction can be completed by substituting sand for the sodium sulfate and fitting the Soxhlet with Dean-Stark apparatus.

b) Place the thimble into the toluene charged (300 mL) Soxhlet apparatus.

c) Add any non-aqueous liquid from the multiphase samples to the Soxhlet thimble and cover the thimble with glass wool.

d) Extract the sample:

1) If necessary, adjust the reflux rate to match the rate of percolation through the sand and silica beds until water removal lessens the restriction of toluene flow. Check the apparatus for foaming frequently during the first two hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

2) If applicable, drain the water from the receiver at 1-2 hours and 8-9 hours, or sooner if the receiver fills with water. Reflux the sample for a total of 18-24 hours. Cool and disassemble the apparatus. Record the total volume of water collected.

e) Remove the distilling flask, rinse the receiver with small portions of toluene and add to the flask.

f) Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

g) Concentrate to approximately 10 mL. Remove and allow to cool for 5 minutes.

h) Rinse Snyder column down into the flask with three 2 mL portions of hexane.

i) If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes, combine with the filtrate extract in a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup.

j) If acid washes are not required, transfer the extract through a drying column containing a 10 cm plug of glass wool and sodium sulfate, and combine with the filtrate portion of the extract (if applicable). Rinse the flask with hexane (3 x 30

mL) and add to the drying column. Concentrate to 1 mL using KD and N-evap apparatus and proceed with sample cleanup.

3. Filters and Filter Particulate

a) Mix the filter and particulate with anhydrous sodium sulfate and load into the thimble, add a fresh charge of toluene (300 mL) to the Soxhlet apparatus. Alternatively, the extraction can be completed by substituting sand for the sodium sulfate and fitting the Soxhlet with Dean-Stark apparatus.

b) Add any non-aqueous liquid from the multiphase samples to the Soxhlet thimble and cover the thimble with glass wool.

c) Extract the sample:

1) If necessary, adjust the reflux rate to match the rate of percolation through the sand and silica beds until water removal lessens the restriction of toluene flow. Check the apparatus for foaming frequently during the first two hours of extraction. If foaming occurs, reduce the reflux rate until foaming subsides.

2) If applicable, drain the water from the receiver at 1-2 hours and 8-9 hou. sooner if the receiver fills with water. Reflux the sample for a total of 18-24 hours. Cool and disassemble the apparatus. Record the total volume of water collected.

d) Remove the distilling flask and rinse the receiver with small portions of toluene and add to the flask.

e) Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

f) Concentrate to approximately 10 mL. Remove and allow to cool for 5 minutes.

g) Rinse Snyder column down into the flask with three 2 mL portions of hexane.

h) If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes, combine with the filtrate in a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup.

i) If acid washes are not required, transfer the extract through a drying column containing a 10 cm plug of glass wool and sodium sulfate, and combine wit. filtrate portion of the extract (if applicable). Rinse the flask with hexane (3 x 30

mL) and add to the drying column. Concentrate to 1 mL using KD and N-evap apparatus and proceed with sample cleanup.

4. Fly Ash Samples

a) Place each prepared fly ash sample into a thimble and place in the Soxhlet apparatus.

b) Add 300 mL toluene and extract for 16-18 hours, maintaining three cycles per hour.

c) Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

d) Concentrate to approximately 10 mL. Remove and allow to cool for 5 minutes.

e) Rinse Snyder column down into the flask with three 2 mL portions of hexane.

f) If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes, transfer the extract to a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup.

g) If acid washes are not required, transfer the extract through a drying column containing a 10 cm plug of glass wool and sodium sulfate, and combine with the filtrate portion of the extract (if applicable). Rinse the flask with hexane (3 x 30 mL) and add to the drying column. Concentrate to 1 mL using KD and N-evap apparatus and proceed with sample cleanup.

5. Soil/Solid Samples

a) Place the prepared sample in the thimble into the Soxhlet extractor. The Dean-Stark attachments maybe utilized in place of the sodium sulfate drying step.

b) Add 300 mL of toluene and reflux for 16-18 hours. Cycle at a rate of three cycles per hour. If applicable, drain the water from the receiver as needed. Record the total amount of water collected.

c) Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

d) Concentrate to approximately 10 mL. Remove and allow to cool for 5 minutes.

e) Rinse Snyder column down into the flask with three 2 mL portions of hexane.

f) If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes, transfer the extract to a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup.

g) If acid washes are not required, transfer the extract through a drying column containing a 10 cm plug of glass wool and sodium sulfate, and combine with the filtrate portion of the extract (if applicable). Rinse the flask with hexane (3 x 30 mL) and add to the drying column. Concentrate to 1 mL using KD and N-evap apparatus and proceed with sample cleanup.

6. Water Samples

a) Add 60 mL of methylene chloride to the sample bottle, cap and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel containing the sample and shake vigorously for two minutes, with frequent venting.

b) Allow the phases to separate for 10 minutes. If the emulsion between layers greater than one-third of the volume, apply mechanical techniques to comp separation.

c) Pass the solvent layer through glass chromatography drying column that contains a pre-rinsed glass wool plug and 5 g of anhydrous sodium sulfate into a K-D flask.

d) Repeat the extraction twice more with fresh portions of methylene chloride and transfer as described above. Discard the water down the drain, flushing with running water,

e) Rinse empty separatory funnel three times with fresh 20 mL aliquots of methylene chloride and pass each aliquot through the column. Combine the extracts and rinsates into the K-D flask.

f) Add a pre-rinsed boiling bead and concentrate on steam bath to between 5 and 10 mL. DO NOT CONCENTRATE TO DRYNESS. Allow to cool 10 minutes.

g) Rinse the Snyder column and KD twice with 5 mL portions of hexane and concentrate to 1 mL on the N-evap.

h) Determine the original sample volume by weighing the sample bottle before after extraction, or by filling the sample bottle with water to the mark. Rec volume to the nearest 5 mL.

i) Proceed to the sample cleanup steps.

7. Milk and Milk Product Samples

a) Add 300 mL of 1.5M potassium oxalate solution and 600 mL of de-ionized water to each sample in the separatory funnel.

b) Gently shake the separatory funnel for 8-10 minutes.

c) Add 150 mL of 1:1:1 ethanol/ether/hexane to the sample and shake gently for 3-4 minutes.

d) Allow the layers to separate 15-20 minutes.

e) Collect the milk (bottom layer) and emulsion layers in a clean 2 L beaker. (The emulsion layer can be reduced by adding small volumes (10-30 mL) of the 1:1:1 solvent mixture to the separatory funnel after separation of the layers.)

f) Transfer the clear organic layer directly to a Kuderna-Danish concentrator and set aside.

g) Transfer the milk and emulsion back to the separatory funnel and repeat the extraction two more times. Combine the organic layers to the K-D flask and save the emulsion layer in a 500 mL separatory funnel.

h) After the final extraction, rinse the 2 L separatory funnel with 60 mL of the 1:1:1 solvent mixture and add to the K-D flask.

i) Concentrate the extract to 2 mL and allow to cool.

j) Quantitatively transfer the extract into the separatory funnel containing the emulsion and add 80 mL hexane.

k) Perform the acid washes and cleanup as described. For milk samples, acid cleanup is not considered optional.

NOTE: The first acid wash should not be shaken. Slowly pour the first 50 mL of sulfuric acid into the separatory funnel and allow to separate for 15 minutes. Drain the acid and perform the remaining washes in the normal manner.

8. Tissue Samples

a) Place the loaded thimble into the Soxhlet apparatus.

b) Add 250 mL of hexane/methylene chloride (1:1 v/v) and reflux for 16-18 hours.

c) Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

d) Concentrate to approximately 10 mL. Remove and allow to cool for 5 minutes.

e) Rinse Snyder column down into the flask with three 2 mL portions of hexane.

f) Perform the acid washes and cleanup as described. For tissue samples, acid cleanup is not considered optional.

NOTE: The first acid wash should not be shaken. Slowly pour the first 50 mL of sulfuric acid into the separatory funnel and allow to separate for 15 minutes. Drain the acid and perform the remaining washes in the normal manner.

g) If acid washes are not required, transfer the extract through a drying column containing a 10 cm plug of glass wool and sodium sulfate, and combine with the filtrate portion of the extract (if applicable). Rinse the flask with hexane (3 x 30 mL) and add to the drying column. Concentrate to 1 mL using KD and N-e apparatus and proceed with sample cleanup.

h) Alternatively, the sample can be extracted using Soxhlet Dean-Stark apparatus and toluene. No sodium sulfate is used with this option.

D. Extract Enrichment

1. Back Extraction with Acid - Microscale

NOTE: This enrichment step is optional. It is used on extracts based on appearance and color. If the extract is cloudy, emulisive, or multi-layered, this back extraction is employed. It is also used when the extract is not clear or if the sample appears particularly dirty (i.e. multi-layer, sludge-like) or contains various organic materials (i.e. milk, fish, vegetation, etc.). Most samples undergo this procedure.

a) Spike each extract with 250 mL of the clean-up std. Prior to concentration using KD and N-evap apparatus.

b) Quantitatively transfer H_2O and soxhlet extracts with 15 mL of hexane to 40 mL vials. Extracts obtained using the ASE method should be concentrated to almost dryness (~1mL) and 15 mL of hexane added.

c) Partition the extract against 2-3 mL concentrated sulfuric acid. Shake for tw minutes with periodic venting into a hood. Remove and discard the acidic

bottom layer. Emulsions may be broken down by mechanical or chemical means.

d) Repeat c, the acid washing, until no color is visible in the aqueous layer, to a maximum of four washings.

e) Acid waste is collected, then stored in labeled containers for disposal. Use caution when handling.

f) Repeat step c, but substitute buffer solution (100 mL 0.5 M KH_2PO_4).

g) Concentrate extract to approximately 1 mL on the N-evap and proceed with column cleanup. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS!

2. Back Extraction with Acid – Macroscale

NOTE: This enrichment step is optional. It is used on extracts based on appearance and color. of the extract is cloudy, emulsive, or multi-layered, this back extraction is employed It is also used when the extract is not clear or if the sample appears particularly dirty (i.e. multi-layer, sludge-like) or contains various organic materials (i.e. milk, fish, vegetation, etc.). Most samples undergo this procedure.

a) Spike the separatory funnel with 250 µL of the cleanup standard (CCl4-#).

b) Quantitatively transfer and partition the extract in 1N-sodium hydroxide. Shake for two minutes with periodic venting into a hood. Remove and discard the aqueous bottom layer. Emulsions may be broken down by mechanical or chemical means. The sodium hydroxide wash may be omitted at the discretion of the technician.

c) Only one NaOH rinse is needed.

d) Partition the extract against 50 mL of the 5%(w/v) sodium chloride solution in the same way and number of repetitions as with base. Discard the aqueous layer.

e) Quantitatively transfer and partition the extract in 50 mL concentrated sulfuric acid. Shake for two minutes with periodic venting into a hood. Remove and discard the aqueous bottom layer. Emulsions may be broken down by mechanical or chemical means.

f) Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.

g) Partition the extract against 50 mL of the 5%(w/v) sodium chloride solution in the

same way as with acid. Discard the aqueous layer.

h) Acid waste is collected, then stored in labeled containers for disposal. Use caution when handling.

i) Pour the extract through a drying column containing 7 to 12 cm of anhydrous sodium sulfate and a pre-rinsed glass wool plug. Rinse the separatory funnel with three 20 mL portions of hexane and add to the column. Collect the extract in a 500 mL KD evaporator flask.

j) Add 1 to 2 clean boiling chips to the receiver and attach a three ball macro Snyder column. Preset the column by adding approximately 1 mL of hexane through the top. Place the KD apparatus in a hot water bath so the entire lower rounded surface of the flask is bathed in steam.

k) Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS.

l) When the liquid has reached an apparent volume of 1 mL, remove the apparatus from the steam bath and allow to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane.

m) Remove the concentrator tube from the apparatus, concentrate to approximately 1 mL on the N-evap and proceed with column cleanup.

3. Silica Column

a) Vertically clamp a disposable glass column, 12 mm ID x 35 cm. Rinse three times with hexane, air dry, and place a pre-extracted silanized glass wool plug into bottom.

b) Pack the column in the following order (bottom to top): 1 g neutral silica, 2 g basic silica, 4 g acidic silica and 2 g neutral silica. Between each layer, tap the column to settle the silica. Wet column with 10 mL hexane after the basic silica layer is added. Plug the end of the column with a septa when it starts dripping. Check the column for channeling. If channeling is observed, discard the column. DO NOT allow the column to go dry.

c) Spike the extract with the cleanup standard (CCl4-#), if it has not already been added.

d) Quantitatively transfer the sample extract onto the column using 2-2 ml rinses of

hexane. Break off the tip of the column containing the septum. Elute until the solvent just covers the silica. Do NOT let the column go dry.

e) Elute the column with 90 mL hexane. Collect the eluant in a 100 mL beaker.

f) Concentrate the extract to approximately 1 mL using KD and N-evap apparatus or ambient air conditions.

g) An equivalent silica column may be substituted so long as the data meet method requirements.

h) Problematic matrices (i.e., adipose tissue, waste samples, etc.) may be processed by mixing up to 100 grams of acid silica into the sample extract. The extract should then be processed through the above silica column and remaining cleanup steps.

4. Alumina Column

a) Pack a silanized glass wool plug into the bottom of a disposable glass column (12 mm ID x 35 mm). Pack the column in the following order: 4 g of anhydrous sodium sulfate, 4 g of neutral alumina, and 4 g of anhydrous sodium sulfate to cover the alumina. Between layers, tap the top of the column gently to settle the adsorbents.

b) Elute with 10 mL hexane. Plug the bottom of the column with a septum just before exposure of the sodium sulfate layer to the air. Discard the eluate. Check the column for channeling. If channeling is present, discard the column. DO NOT TAP A WETTED COLUMN AND DO NOT LET THE COLUMN GO DRY.

c) Quantitatively transfer the sample to the top of the column with 2-2 ml of hexane. Elute the sample with 20 mL hexane to complete the transfer of the sample cleanly to the surface of the alumina. Archive the eluate until after sample analysis.

d) Elute with 20 ml of 60% (v/v) methylene chloride in hexane and collect this fraction in an 8 dram vial.

e) Concentrate the extract to near dryness using an N-evap apparatus.

f) An equivalent alumina column may be substituted so long as the data meet method requirements.

5. Carbon Column

a) Prepare carbon/Celite packing by mixing 18% (by weight) 100-400 mesh active carbon (pre-washed in methanol and dried in a vacuum oven at 110°C) and 82%

(by weight) Celite. Mix thoroughly.

b) Bake the mixture at 130°C for 6 hours. Store in desiccator.

c) Prepare an 8 mm glass tube about one foot in length. Rinse the tube three times with 1 mL portions of hexane.

d) Insert a silanized glass wool plug at one end and pack with 1 cm of Celite followed by 0.5 g of the carbon/Celite mixture. Cap the end with a silanized glass wool plug.

e) Rinse the column "clean (Celite)" side up sequentially with 5 mL of toluene, 2 mL of methylene chloride/methanol/toluene (75:20:5 v/v), 2 mL of cyclohexane/methylene chloride (1:1 v/v) and 5 mL hexane. The flow rate should be less than 0.5 mL/minute. If the flow rate is greater than 0.5 mL/minute, discard the column. Discard the rinses.

f) While the column is still wet with hexane, quantitatively transfer the sample extract to the top of the column with two 2 mL aliquots of hexane.

g) Elute the column sequentially with 2 mL of cyclohexane/methylene chloride 1 v/v) and 2 mL of methylene chloride/methanol/toluene (75:20:5 v/v). Ar e these eluates until after sample analysis.

h) Turn the column upside down and elute the PCDDs and PCDFs with 30 mL of toluene. If carbon is present in the eluate, filter through a 0.45 µm glass fiber filter rinsing with an additional 2 mL of toluene.

i) An equivalent carbon column may be substituted so long as the data meet method requirements

6. Florisil Column (Optional, can be performed on final extract if necessary, under the authorization of the GC/MS analyst.)

a) Prepare a column (same dimension as alumina column) by inserting a silanized, pre-extracted glass wool plug. Add 1.5 g of activated Florisil topped with a 1 cm layer of anhydrous sodium sulfate.

b) Pre-elute the column with 20 mL of methylene chloride, followed by 10 mL of hexane. Discard eluants.

c) Quantitatively transfer the extract to the top of the column with 2 mL of hexane.

d) Elute the column with 20 mL of methylene chloride (2% v/v) in hexane. Cc this fraction in a pre-rinsed 8 dram glass vial. Set aside. It may be used as a test

of column efficiency.

e) Elute the column with 50 mL of methylene chloride. Collect this fraction in a pre-rinsed 100 mL beaker. Concentrate under a gentle stream of nitrogen to less than 5 mL. Proceed to final extraction preparation.

E. Final Extract Preparation

1. Extract Transfer

a) Concentrate the extract under a gentle stream of nitrogen to a volume of less than 1 mL. Do NOT blow the sample so the portions of the solvent "ride" up the sides of the glass vial.

b) Add 10 µL of tridecane to an autosampler vial to act as a keeper solvent.

c) Quantitatively transfer the extract to the autosampler vial. Rinse the original vial with less than 1 mL of methylene chloride/hexane (60:40 V:V). Transfer rinsate to the autosampler vial. Repeat rinse of the autosampler vial with two additional aliquots (<1 mL) of methylene chloride/hexane. Then blow down extract to the level of the 10 uL keeper solvent.

d) Add the 10 µL of recovery standard (CR3-#) to the extract and cap. Vortex each sample vial.

e) Transfer the extracts to the analytical laboratory for analysis. Extracts should be stored in the dark at approximately 4°C.

F. Instrument Maintenance

1. There is no set schedule for the maintenance listed in this section. It is performed on an as needed basis. Regular preventative maintenance is performed by Pace Analytical's service engineer. If the instrument needs to be vented, do the following in this order: close the analyzer isolation valve, turn off the source ion gauge, close the source isolation valve, close all source rough pump valves, allow air into the source chamber through the bleed valve while watching vacuum gauges to ensure leakage does not occur. If any leakage is seen, close the bleed valve and open the main roughing pump valve. Determine the cause of the problem and correct.

2. The rough pump oil should be changed if the pump fails to produce a vacuum lower than 10^{-1} mbar or if the pump oil becomes excessively dark. To do so, turn off the ion gauge, isolate and turn off the diffusion pump and allow it to cool. When the diffusion pump is cool, isolate and turn off the rough pump. Now drain the oil into a waste container and recap the drain. Add oil up to the full line and turn on the pump. When the gurgling sound stops, open the valve to pump on the instrument. After several

minutes, turn on the diffusion pump. Wait another 10-15 minutes and turn on the ion gauge. If it is a source linked pump, the source will need to be evacuated.

3. When the carrier gas, helium, pressure gets below 500 psi, the tank should be replaced.

4. The chromatographic column used for these analyses is the DB-5MS in a 60 meter length. As with any column, these will degrade in time. Once this degradation reaches the point where EPA Method 8290 criteria are not met, the column needs to be replaced. Similar results are required for the DB-225 confirmation column.

G. Sample Analysis

Introduce PFK into the batch inlet and tune the instrument to a resolution of ≥ 10,000 (M/ΔM, 10% valley) using a PFK peak within the analysis mass range (M/Z 331 or 381).

Typical Operating conditions include:

Trap current: 500-700 μA
Electron Energy: 32 ± 5 eV
Source Temperature: 270 °C
Emmision/Trap Ratio: ≤ 3
Accelerating Voltage: 8000 eV

After calibration and column performance have been established, (per Quality Control Section Guidelines) any spikes are typically analyzed. A blank must be analyzed between calibration standards and client samples.

H. Data Processing

1. The raw data files are imported into the AutoPro data processing program for integration. Information on how to use AutoPro is available in the AutoPro manual that can be accessed on the HRMS group computers. Also, since the DB-5MS capillary column gives partial resolution of 2,3,7,8-TCDF isomer (typically 30-40% valley), second column confirmation analyses are only performed if coelution is exhibited or based upon project requirements.

2. Note that the window mixture does not need to be queued. Visually inspect the chromatographic data to ascertain the elution times of the first and last eluting isomers of each congener class and chromatographic resolution.

   a) With the elution time information recorded, adjust the method file times so that the group changes occur at points between the elution time of the last isomer of a given class and the first isomer of the following class. The first PeCDF isomer is monitored in Group 1 with the group change set approximately 30 seconds later.

I. CALCULATIONS

1. The PCDD/PCDF isomers (native or labeled) are quantified by comparison of their responses to those of the corresponding/appropriate labeled standard. Relative response factors are calculated from analyses of standard mixtures containing representatives of each of the PCDD/PCDF congener classes at five concentration levels, and each of the internal and recovery standards at one concentration level. The PCDD/PCDF response factors are calculated by comparing the sum of the responses from the two ion masses monitored for each chlorine congener class to the sum of the responses from the two ion masses of the corresponding isotopically labeled standard. The formula for the response factor calculation is:

$$Rf = \frac{Aa \times Qs}{As \times Qa}$$

Where:

Rf = Response factor
Aa = Sum of integrated areas for analyte
Qs = Quantity of labeled standard
As = Sum of integrated areas for labeled standard
Qa = Quantity of analyte

2. The levels of PCDD/PCDF in the samples are quantified using the following equation:

$$C = \frac{An \times Qis}{Ais \times W \times Rf}$$

Where:

C = Concentration of target isomer or congener class
An = Sum of integrated areas for the target isomer or congener class
Qis = Quantity of labeled internal standard added to the sample
Ais = Sum of integrated areas for the labeled internal standard
W = Sample amount
Rf = Response factor

3. A method detection limit (MDL), based on the signal to noise ratio of the noise level of the ion of interest versus the appropriate standard, is calculated for each sample and isomer. The equation used for calculating the MDL is:

$$MDL = \frac{Hn \times Qis \times 2.5}{His \times W \times Rf}$$

Where:

MDL = Method Detection Limit
Hn = Sum of noise heights for target isomer

Qis = Quantity of labeled internal standard added to the sample
His = Sum of signal heights from labeled internal standard
W = Initial sample weight or volume
Rf = Response factor

Note: If a signal is present which does not meet the ion ratio requirement but is greater than 2:5:1 S/N, the 2.5 factor is omitted for that ion mass.

4. A lower reporting limit equal to 1/5 of the concentration of the lowest calibration standard is used for this method and is calculated as follows:

$$LRL = \frac{0.2C \times V}{W}$$

Where:
LRL = Lower Reporting Limit
C = Concentration of lowest level standard
V = Volume of final extract
W = Initial sample weight or volume

Isomers present below the LRL are reported as not detected at the LRL. If the calculated MDL is above the LRL for any given isomer, the signal to noise based MDL is reported for that isomer. If requested by a client, the MDL values may be reported for all analytes. Any positive values below the concentration of the lowest calibration standard (above equation without the 0.2 factor) will be flagged "J" as estimated values.

5. The recovery of the 2,3,7,8-TCDD-$^{37}Cl_4$ enrichment efficiency standard and each $^{13}C_{12}$-labeled internal standard, relative to either 1,2,7,8-TCDD-$^{13}C_{12}$ or 1,2,3,7,8,9-HxCDD-$^{13}C_{12}$, is calculated using the following equation:

$$\%R = \frac{Ais \times Qrs \times 100}{Rfr \times Ars \times Qis}$$

Where:
%R = Percent recovery of labeled internal standard
Ais = Sum of integrated areas of labeled internal standard
Qrs = Quantity of recovery standard
Ars = Sum of integrated areas of recovery standard
Rfr = Response factor of the specific labeled internal standard relative to the recovery standard
Qis = Quantity of the labeled internal standard added to the sample

XIII. QUALITY CONTROL

A. The quality of the sample processing steps and instrument performance are monitored on a routine basis. The procedures and criteria are summarized below.

1. Internal standards are spiked into each sample prior to extraction in order to monitor the level of recovery that is achieved for each individual sample. Acceptable recoveries range from 40 to 135% for the internal standards unless a deviation is due to variation in instrument response as a result of analytical interferences. Results outside the target range must be flagged. The analysis may be repeated based on project requirements.

2. Prior to each analysis, the resolution of the mass spectrometer is verified to be 10,000 or greater. Hardcopies of the reference peaks are printed at the beginning and end of each analytical shift. The resolving power of the DB-5MS chromatographic column is checked daily using a standard solution containing 2,3,7,8-TCDD and the adjacent TCDD isomers. When second column confirmations are performed, the DB-225 (or equivalent) column resolution is checked using a standard solution containing 2,3,7,8-TCDF and the adjacent TCDF isomers. Acceptable performance is achieved when 2,3,7,8-TCDD or 2,3,7,8-TCDF is resolved from the adjacent isomers by a valley of 25% or less. The group times for the selected-ion-monitoring data acquisitions are also checked daily by analyzing the column performance mix that contains the first and last eluting isomers of each congener class. In this way one is assured of collecting data representative of the total PCDD/PCDF content and the 2,3,7,8-substituted isomers are suitably resolved. The isomers described above are also available as part of the CS-3 calibration solution (EPA 1613 CS3 WT).

3. Initial calibrations are generated using standard solutions containing target native and labeled PCDD/PCDF compounds. Response factors are calculated and averaged for each compound. These averages are used for quantification and for comparison to the daily continuing calibration. The relative standard deviation for each native compound must be 20% or less (30% or less for the labeled compounds) as specified in SW 846 Method 8290. A continuing calibration standard is analyzed at the beginning and end of each 12-hour shift on days when initial calibrations are not performed. The initial calibration is considered to be valid when the response factors from the continuing calibration analysis agree to within ± 20% (±30% for the labeled compounds) of the average from the initial calibration.

B. Samples are queued as discussed in the data processing section of this SOP. In order for a peak to be accepted as a PCDD/PCDF isomer, the following criteria must be met:

1. Intensity ratios must be within 15% of the corresponding standard.

2. The signal to noise of the peak versus the background noise must be >2.5:1.

3. No PCDF peak may have a co-eluting peak in the mass window monitored for polychlorinated diphenylethers.

4. The peak elutes within the retention time determined from the analysis of the column performance window mix standard.

C. Data Acceptance/Rejection Criteria and Corrective Action

1. Method Blank

a) One method blank is typically prepared with each twenty samples of any given matrix.

b) A method blank or solvent blank must be analyzed between standards and samples to demonstrate lack of PCDD/PCDF carryover.

c) If the blank contains PCDDs/PCDFs, find and correct the source of the problem.

1) If the contamination appears to be instrument related, correct the problem, analyze a solvent blank, and reanalyze the method blank before proceeding with samples.

2) If the contamination appears to be from the extraction or enrichment ster the analysis of samples may continue. If the sample shows similar contamination it should be re-extracted, if possible. All associated sample results will be qualified for blank contamination when any analyte is detected in the method blank at 10% of more of the sample concentration.

3) If the blank shows no contamination above the levels of the lowest calibration solution, analysis of samples may continue. However, all associated sample results will be qualified for blank contamination when any analyte is detected in the method blank at 10% of more of the sample concentration.

2. Laboratory Control Spike

a) One laboratory control spike is prepared with each ten samples of any given matrix. The recoveries of the native PCDD/PCDF analytes in the spiked samples generally range from 70 to 130.

NOTE: Recoveries of up to 2 native analytes outside the acceptable range do not invalidate the data but provide information which is used by the laboratory to monitor recovery trends and to assure optimization of the method. Any failure can not occur for the same set of analytes in two consecutive batches. Affected samples will be re-extracted and reanalyzed if possible, or the data will be qualified with a detailed explanation of data impact in the narrative section the final report

b) Accuracy of the standard spiking solutions should, at a minimum, be verified quarterly by comparison of the solutions to certified native materials obtained from a second source or batch.

3. Matrix Spike/Matrix Spike Duplicate

a) One matrix spike/spike duplicate set may be prepared with the extracted sample batch. The recoveries of the native PCDD/PCDF analytes in the spiked samples generally range from 70 to 130 when not affected by levels or interferences present in the sample material.

NOTE: Recoveries of selected analytes outside the acceptable range do not invalidate the data but provide information which is used by the laboratory to monitor recovery trends and to assure optimization of the method. This is particularly true of MS/MSD recoveries where native PCDD/PCDF are subject to the affects of the sample source.

If native recoveries in the MS/MSD indicate a laboratory method performance problem (i.e. >2 recoveries are outside the acceptance limits, but the original sample does not appear to be the cause), analysis of the associated batch samples will be suspect until corrective action is taken to determine the root cause of the problem, and the problem is negated.

b) Accuracy of the standard spiking solutions should, at a minimum, be verified quarterly by comparison of the solutions to certified native materials obtained from a second source or batch.

c) Control limits are determined on an annual basis, or sooner if methodology changes occur. Representative data points are then plotted on a regular basis to provide an ongoing comparison to the statistical ranges.

D. REPORTING AND REVIEW

Reports are prepared using previous reports as templates and making modification as appropriate. The amount of information included with the report is determined based on the client requirements.

1. Units/Significant Figures

a) Values are reported to two significant figures. Aqueous samples are routinely reported in units of ng/L and solid matrices are reported in ng/Kg. Other units are available upon request.

2. Data Qualifiers/Flags

a) The information typically reported is summarized below.

1) Base Report

(a) Case Narrative including client name, address, and project information, introduction, sample information and discussion of results.

(b) Copies of chain of custody documents and analytical requests

(c) Sample Analysis Results

2) Full Report

(a) Those items listed in base report summary

(b) Methodology, including example calculations and QA/QC summary.

(c) Raw data including sample, QC sample and standards

(d) Selected ion current profiles (chromatograms)

(e) Communications records

(f) Extraction and login forms

(g) Instrument resolution checks

(h) Calibration Results

3. Those items included in the report may be tailored to the clients requirements and may not fit into the above stated categories. A checklist is available to assure completeness of full reports (Attachment 5).

4. Levels of Review

a) Each sample work-up must be rechecked for work-up, header information and data entry accuracy. The results of this review are recorded on the raw data sheet.

b) All data generated during analysis are reviewed by the project manager prior to inclusion in the final report. The final report is reviewed, minimally, by two senior technical staff members and a review checklist is completed.

5. Data Archiving or Filing

a) Initial and Continuing Calibration standard data are stored in a QA notebook located near each instrument.

b) After reporting, the complete project file is archived by in the permanent chemistry archive.

XIV. METHOD PERFORMANCE

A. There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications may be found in the Laboratory Quality Manual and specific Standard Operating Procedures.

1. The analyst must read and understand this procedure with written documentation maintained in his/her training file.

2. An initial demonstration of capability (IDC) must be performed. A record of the IDC will be maintained in his/her file with written authorization from the Laboratory Manager and Quality Assurance Officer.

3. An annual minimum detection limit (MDL) study will be completed for this method and whenever there is a major change in personnel or equipment.

4. Periodic performance evaluation (PE) samples are analyzed to demonstrate continuing competence.

XV. POLLUTION PREVENTION AND WASTE MANAGEMENT

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. The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

C. The Environmental Protection Agency (USEPA) requires that laboratory waste management practice 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 waster 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 MN SOP MN-C-701.

XVI. REFERENCES

USEPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Method 8290, November, 1992

USEPA Method 1613: Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS (October 1994, Revision B).

ATTACHMENT I

Pace Analytical

DIOXIN EXTRACTION WORKSHEET

Method (Circle One): EPA 8290 Method 1613 TO9 Method 23 Matrix: PUF XAD Solid Water Tissue Other: _____ Page ____ of ____

Client(s): _____ HPN(s): _____

Date Extraction On: _____ Time On: _____ Date Extraction Off: _____ Time Off: _____

	Sample #	Standards	L or g Extracted	Filtered (Y/N)	Cl-37 Std Mineral Oil	Acid/ Base/ NaCl	Silica Date: ____ Init: ____ Temp ____	Alumina Date: ____ Init: ____ Temp ____	Carbon Date: ____ Init: ____ Temp ____	Res Std	Glassware Set	Comments
1						B A	Hex Lot#:	Hex Lot#:	Toluene Lot#:			
2						B A	Humidity:	60% Batch#:	75% Batch#:			
3						B A		Humidity:	50% Batch#:			
4						B A			Hex Lot#:			
5						B A			Humidity:			
6						B A						
7						B A						
8						B A						
9						B A						
10						B A						
11						B A						
12						B A						

Extract Solvents:
Toluene Lot # _____
Hexane Lot # _____
Methylene Chloride Lot # _____

Acid Base:
Sulfuric Acid Lot # _____
Base Batch # _____
NaCl Batch # _____

Silica:
Neutral Batch # _____
Basic Batch # _____
Acid Batch # _____

Internal Std _____
Cl-37 Std _____
Recovery Std _____
Tridecane _____

Native _____
Others _____
Alumina Lot _____

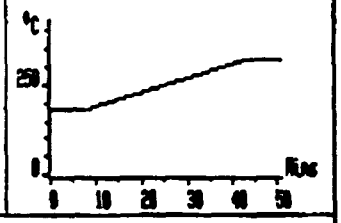
Extracts Relinquished By: _____ Received By: _____ Date: _____

KEY: A = Internal Standard Added [illegible]

ATTACHMENT II

SYSTEM: [illegible] (GCC) Update Parameters 14-JUN-99 Page 1 of 2

Temperature Ramp Parameters			Acquisition Parameters	
TE1 Temperature 1	(°C)	100	INO Instrument number	1
TI1 Time 1	(mins)	0.00	ACT Acquisition type	STR
RE1 Rate 1	(°C/min)	4.0	ACS Acquisition system	[illegible]
TE2 Temperature 2	(°C)	320	DNT Datafile name	[illegible]
TI2 Time 2	(mins)	0.00		
RE2 Rate 2	(°C/min)	0.0		
TE3 Temperature 3	(°C)	0		
TI3 Time 3	(mins)	0.00		
RE3 Rate 3	(°C/min)	0.0		
TE4 Temperature 4	(°C)	0		
TI4 Time 4	(mins)	0.00		
RE4 Rate 4	(°C/min)	0.0		
TE5 Temperature 5	(°C)	0		
TI5 Time 5	(mins)	0.00		



?=help RETURN=next ESC=previous %=exit CTRL/A=abort %=hardcopy
@=quit @=go "name"=select <=page >=page @=create

SYSTEM: [illegible] (GCC) Update Parameters 14-JUN-99 Page 2 of 2

Gas Chromatograph Parameters			Detector + Signal Parameters		
GCT Gas chromatograph type		HP5890	DET Detectors	[-/A/B/AB]	-
[illegible] Maximum oven temperature		350	DTA Detector A temperature (°C)		100
[illegible] Cryogenic cooling	[Y/N]	NO	DTB Detector B temperature (°C)		100
[illegible] Equilibrium time	(mins)	0.20	SA1 Signal 1 allocation		A
[illegible] Valve program		3	SR1 Signal 1 range	(2in nV)	0
[illegible] Valve time	(mins)	1.00	SZ1 Signal 1 zero level		0.0
[illegible] Pump valve	[Y/N]	NO	SA2 Signal 2 allocation		B
[illegible] Pump time		0.00	SR2 Signal 2 range	(2in nV)	0
INJ Injector	[A/B]	B	SZ2 Signal 2 zero level		0.0
LJT Injector temperature	(°C)	275			

Autosampler Parameters					
NOS Number of samples		1	SWA Sample wash	[Y/N]	YES
NOI Number of injections		1	PWA Post wash	[Y/N]	NO
SVB Start bottle		1	RTS Autosampler	[Y/N]	NO

?=help RETURN=next ESC=previous %=exit CTRL/A=abort %=hardcopy
@=quit @=go "name"=select <=page >=page @=create

ATTACHMENT III

[illegible] Parameters for Selective Ion Recording [GR 1 EVE] (Sector)

DAT	Data filename	0-0		DAV	Maximum volts						10000
REF	Reference filename	PFK		DAM	Maximum mass at DAV						2350
INS	Instrument	1:70-250SE		GTR	Time 0:12:00 0-29-29 Mode EI+15 Gas						
ACN	Customer account			CHN	M(amu)	S(ms)	D(ms)		M(amu)	S(ms)	D(ms)
ACV	Monitoring volts	0000		A	303.5816	55	15	H	375.8367	55	15
RES	Instrument resolution	10000		B	305.8507	55	15				
SMP	#Samples	1		C	315.5418	55	15				
INJ	#Injections	1		D	317.5309	55	15				
GRP	#Groups	5		E	318.5793	55	15				
CLS	#Calibration scans	0		F	318.5793	50	15				
CST	Cal. scan time (s)	10		G	319.8555	55	15				
CTL	Cal. tolerance (ppm)	50		H	321.8536	55	15				
CEX	Cal. examination	Y		I	327.8047	55	15				
PEX	Peak examination	Y		J	331.5367	55	15				
LOS	Lock span (peak widths)	2.0		K	333.5338	55	15				
LST	Lock step (peak widths)	0.02		L	339.8507	55	15				
FLO	Fast Lock on	Y		M	341.8567	55	15				

TXT Sampled 1: CS-3 (121500-10)

'I-sort names 'W-write/copy RETURN-next ESC-prev CTRL/P-abort
'Dup 'Dupl 'Duplate 'DEL-delete 'O-overwrite 'Trans <group,sample>

[illegible] Parameters for Selective Ion Recording [GR 2 EVE] (Sector)

DAT	Data filename	0-0		DAV	Maximum volts						10000
REF	Reference filename	PFK		DAM	Maximum mass at DAV						2350
INS	Instrument	1:70-250SE		GTR	Time 0:29:32 0-30-32 Mode EI+15 Gas						
ACN	Customer account			CHN	M(amu)	S(ms)	D(ms)		M(amu)	S(ms)	D(ms)
ACV	Monitoring volts	0000		A	339.8507	55	20				
RES	Instrument resolution	10000		B	341.8567	55	20				
SMP	#Samples	1		C	351.8509	55	20				
INJ	#Injections	1		D	353.8569	55	20				
GRP	#Groups	5		E	354.5792	55	20				
CLS	#Calibration scans	0		F	354.5792	55	20				
CST	Cal. scan time (s)	10		G	355.8546	55	20				
CTL	Cal. tolerance (ppm)	50		H	357.8517	55	20				
CEX	Cal. examination	Y		I	367.8948	55	20				
PEX	Peak examination	Y		J	369.8910	55	20				
LOS	Lock span (peak widths)	2.0		K	409.7594	55	20				
LST	Lock step (peak widths)	0.02									
FLO	Fast Lock on	Y									

TXT Sampled 1: CS-3 (121500-10)

'I-sort names 'W-write/copy RETURN-next ESC-prev CTRL/P-abort
'Dup 'Dupl 'Duplate 'DEL-delete 'O-overwrite 'Trans <group,sample>

ATTACHMENT III (Continued)

```
* SYSTEM:DADFUR      Parameters for Selective Ion Recording [GR 3 KVE] (Sector)

DAT Data filename                 A:0      IAV Maximum volts                    10000
REF Reference filename            PFK      IMR Maximum mass at IAV               2350
INS Instrument            1:70-250SE       GTR Time 0:33:35 0:37:52 Mode EI+IS Gas
ACN Customer account                       CHN  M(amu) S(ms) D(ms)      M(amu) S(ms) D(ms)
ACV Accelerating volts            8000     A  373.8287   55   20
RES Instrument resolution        10000     B  375.8178   55   20
SMP #Samples                         1     C  380.5761   55   20
INJ #Injections                      1     D  380.5761   55   20
GRP #Groups                          5     E  383.8539   55   20
CLS #Calibration scans               0     F  385.8610   55   20
CST Cal. scan time (s)              10     G  389.8156   55   20
CTL Cal. tolerance (ppm)            50     H  391.8127   55   20
CEX Cal. examination                 Y     I  401.8559   55   20
PEX Peak examination                 Y     J  403.8529   55   20
LMS Lock span (peak widths)        2.0     K  445.7955   55   20
LST Lock step (peak widths)       0.02
FLO Fast lock on                     Y

TXT Sample# 1:  CS-3 (121598-1A)

'I'=start masses '%'=hardcopy RETURN=next ESC=prev CTRL/A=abort
'S'=go 'Q'=quit 'C'=create 'DEL'=delete 'O'=overwrite '?'=zero <group,sample>
```

```
* SYSTEM:DADFUR      Parameters for Selective Ion Recording [GR 4 KVE] (Sector)

DAT Data filename                 A:0      IAV Maximum volts                    10000
REF Reference filename            PFK      IMR Maximum mass at IAV               2350
INS Instrument            1:70-250SE       GTR Time 0:37:55 0:41:29 Mode EI+IS Gas
ACN Customer account                       CHN  M(amu) S(ms) D(ms)      M(amu) S(ms) D(ms)
ACV Accelerating volts            8000     A  380.5761   50   20
RES Instrument resolution        10000     B  380.5761   50   20
SMP #Samples                         1     C  407.7818   55   20
INJ #Injections                      1     D  409.7788   55   20
GRP #Groups                          5     E  417.8258   55   20
CLS #Calibration scans               0     F  419.8228   55   20
CST Cal. scan time (s)              10     G  423.7767   55   20
CTL Cal. tolerance (ppm)            50     H  425.7737   55   20
CEX Cal. examination                 Y     I  435.8169   55   20
PEX Peak examination                 Y     J  437.8140   55   20
LMS Lock span (peak widths)        2.0     K  479.7165   55   20
LST Lock step (peak widths)       0.02
FLO Fast lock on                     Y

TXT Sample# 1:  CS-3 (121598-1A)

'I'=start masses '%'=hardcopy RETURN=next ESC=prev CTRL/A=abort
'S'=go 'Q'=quit 'C'=create 'DEL'=delete 'O'=overwrite '?'=zero <group,sample>
```

ATTACHMENT III (Continued)

```
* SYSTEM:OIONFUR    Parameters for Selective Ion Recording (GH 5 KVE) (Sector)

DAT Data filename          A:0      IAV Maximum volts                    10000
REF Reference filename     PFK      IAR Maximum mass at IAV               2350
INS Instrument             1:70-250SE  GTM Tune 0:41:32 0:46:00 Mode EI+IS Gas
ACN Customer account                CHN  M(amu) S(ms) D(ms)     M(amu) S(ms) D(ms)
ACV Accelerating volts     8000     A  438.9728   50   20
RES Instrument resolution  10000    B  438.9728   50   20
SMP #Samples               1        C  441.7428   80   20
INJ #Injections            1        D  443.7398   80   20
GRP #Groups                5        E  453.7830   80   20
CLS #Calibration scans     0        F  455.7801   80   20
CST Cal. scan time (s)     10       G  457.7377   80   20
CTL Cal. tolerance (ppm)   50       H  459.7347   80   20
CEX Cal. examination       Y        I  469.7779   80   20
PEX Peak examination       Y        J  471.7749   80   20
LWS Lock span (peak widths) 2.0     K  513.6775   80   20
LST Lock step (peak widths) 0.82
FLO Fast lock on           Y

TXT Sample# 1:  CS-3 (121598-1A)

'I=sort masses '%=hardcopy RETURN=next ESC=prev CTRL/A=abort
'Grp 'Dupl 'Create 'DEL=delete 'Overwrite 'Z=zero <group,sample>
```

ATTACHMENT IV

Full Validation Package Checklist

Text

_____ Case Narrative
_____ Tables

Appendix A

_____ Chain of Custody
_____ Copy of Airbill
_____ "Blackout" Sheet
_____ Extraction Sheet Copy
_____ Moisture Sheet Copy
_____ HRMS Logbook Page Copies
_____ HRMS Resolution Check Copies (If Requested)

Appendix B

_____ Sample Results

Appendix C

_____ Blank Results
_____ Spike Results
_____ MS/MSD Relative Percent Difference Results
_____ Calibration Results

Appendix D

_____ Sample Chromatograms
_____ Sample Raw Data

Appendix E

_____ Standard Chromatograms
_____ Standard Raw Data

Appendix F

_____ Blank Chromatograms
_____ Spike Chromatograms
_____ Blank Raw Data
_____ Spike Raw Data

Appendix D

APPENDIX D
Response to Comments

CELRN-EC-R-D (200-1c) 21 April 2004

MEMORANDUM FOR CELRN-EC-R-M (Ingram)

SUBJECT: Response to comments from Review of Site Specific Quality Assurance Project Plan, Remedial Investigation, Part 1 at Reservoir Number 2 Burning Ground (2BG), Former Plum Brook Ordnance Works, Sandusky, Ohio, Prepared by Jacobs Engineering Group, Inc., Dated March 2004

Reviewer – Becky Terry

1. **Page 1-1, Section 1.0, Second Paragraph, First Sentence. Correct title for EM 200-1-3 *Requirements for the Preparation of Sampling and Analysis Plans*, U S Army Corps of Engineers.**

Response: Agree. The reference will be corrected.

2. **Page 3-1, Section 3.1.1. See comment 10 from the Site Specific SAP.**

Response: Jacobs performed a thorough review of the available data and based the investigation on the existing data set. Jacobs has since received the EDD from Shaw and will make a determination on the usability of the data for the risk assessment for the Final SAP. If the data quality is not sufficient for the risk assessment, the sampling strategy may need to be revised.

3. **Page 5-1, Section 5.1. MDL's and MRL's that are provided should be specific for the laboratories, methods, and for the matrices of concern.**

Response: The MDLs and MRLs provided are specific for the laboratories, methods, and matrices of concern.

Subject: Response to review comments for the Site-Specific Sampling and Analysis Plan, Remedial Investigation, Part 1, At Reservoir No. 2 Burning Ground (2BG), Former Plum Brook Ordnance Works, Sandusky, Ohio, March 2004, prepared by Jacobs Engineering.

Reviewer Name: Groenjes, Cheryl (Chemistry) – HTRW Center of Expertise

Comment # 1: General. I worked with CRREL recently on an explosives module for the Field Analytical Technology Encyclopedia (FATE) website cosponsored by the Corps and EPA; and have gleaned a few facts from this to share FYI and in support the Site-Specific Definition of Problem presented in section 1-3 and proposed sampling efforts described in sections 3.2.5, 3.2.6. and 5.4. Heat from the burning process sometimes resulted in melting of the energetic material, which penetrate below the surface at burning grounds and resolidify - leading to sometimes pure material in the shallow subsurface. I have attached a picture of subsurface re-crystallization of explosives found between burning trays at an ordnance works facility. Note: The orange-colored soil at the bottom of the pit contains percent levels of TNT. Visual observations should be documented clearly to allow accurate interpretation of sample data, and it's link back to the CSM for the identification of potential sources within the 2BG.

Response: Jacobs has proposed to excavate to 12" below the burn layer and provide visual descriptions of the burn layer and soil beneath the burn layer. Prior trenching performed at the site in 1996 did not identify any pure explosive product, however the reviewers comment is noted and appreciated. Jacobs will carefully observe the soil beneath the burn layer.

Comment # 2: p. FSP 3-5, 3.2.7. Suggest the adoption of field analytics (for nitroaromatics) in an adaptive sampling / analytical strategy to reduce decision error for this site. These techniques can provide general information on a larger number of samples. The greater sample density affords more effective information site-wide for the identification of potential contaminant hot spots outside of the burning pit boundary (currently stated as a decision error that cannot be mitigated due to budget constraints). An integrated analytical strategy provides more information site-wide, and allows the focusing of samples for offsite analyses to locations appropriate for its intended use - i.e., where samples should be taken to support the risk assessment. This approach will be more cost effective for the samples sent for more costly analysis are more meaningful in light of the measurements obtained in the field. Although the field measurements are not typically used within the risk assessment, the information is critical in developing an accurate CSM, and interpreting the fewer (more costly analytical) data. Several techniques, i.e., colorimetric-based, would be able to provide the information needed to focus contingency analyses by the definitive methods.

Response: This approach was not included in the SOW. Such an approach would result in fewer fixed laboratory samples and an increased percentage of drilling costs if used for subsurface delineation. This approach may be appropriate for surface soil hot spots during a subsequent phase of investigation if the risk assessment suggests further action is warranted. Jacobs experience with field test kits for delineation purposes have not been positive, frequently yielding false positives and thus incurring unnecessary stepouts.

Comment # 3: p. FSP 5-3, 1st paragraph. Suggest the use of a project website to communicate issues amongst team members.

Response: A project website does exist, however not all information is available due to security issues.

Comment # 4: QAPP pgs. 3-1 – 3-3, 3.1.1 The analytical protocols designated for surface and subsurface soils is incomplete and in error for the following. It should be noted that different prep methods perform differently. In order to maintain continuity in data obtained to support site characterization, suggest ensuring the protocols noted are complete and documented within the record. Suggest checking with your laboratories to ensure what they will be using to ensure consistency in data obtained between the primary and QA labs also. Update protocols given within each area as follows:

a. Method 3540C is the currently promulgated method for soxhlet.

b. Method 8082 (PCBs) requires the designation of a preparation method.

c. Method 6010C and 7000 series methods for metals requires the designation of a preparation method (typically 3050 or 3051)

Response: Agree. The corrections and additions will be made as requested.

Comment # 5: p. QAPP 3-3, 3.1.2. Due to the discussion covering both SW and sediments, analytical protocols should designate preparatory procedures for both water and soil matrix-types. For instance, VOCs by 8260B in water should require the use of 5030B as an appropriate preparation method. Method 8310 for PAHs in water could use 3510C or 3520C. Regardless, the sample should be analyzed at the pH received. PCBs and metals needs both water and soil prep methods identified. Refer to SW-846 Chapter 2 for further details.

Response: Agree. The appropnate prep methods will be designated for each matrix and analysis.

Comment # 6: p. QAPP 3-4, 3.1.3.

a. The sample handling proposed for the dissolved metals samples is not recommended, and has been shown to induce a low bias in the dissolved metals data. Suggest filtration be done in the field as soon as possible to ensure the validity of the data and avoid rejection of, or suspicion of low bias in the data by the regulatory authority.

b. The preparatory methods included here for VOCs and PAHs do not apply to GW – but are designed for soils. Replace or include appropriate preparatory methods for VOCs, PAHs, and metals.

Response: a) Agree. The text will be amended to indicate that the samples will be filtered in the field.

b) Agree. The prep methods will be amended to reflect the appropriate matrix.

Comment # 7: p. QAPP 3-5, 3.1.4. After the TCLP procedure (1311) is complete, the leachate undergoes a preparation method prior to IDW analyses much like a water sample does. Suggest including the appropriate preparatory method within the analytical protocols.

Response: Agree. The preparatory methods will be added to the text.

Comment # 8: p. QAPP 3-5, 3.2.1. Suggest a review of the SI data be done to identify an initial group of Chemicals Of Potential Concern (COPCs), and then evaluate whether sensitivity for those COPCs is sufficient for the intended comparison to screening values (RBCs). Those COPCs that do not meet sensitivity requirements should be clearly identified and decisions made whether method modifications are possible, needed and then pursued. There are several ways to increase a method' sensitivity. For instance, a larger volume of sample can be processed (i.e., VOCs can undergo a 25 mL purge vs. the 5 mL used, use larger soils sub-samples), the extract can be reduced down further, or an alternative procedure can be chosen that is more amenable to these techniques, etc. However, these types of measures must be coordinated with the lab and focused to improve the usability of critical data points and COPCs only. Suggest these planning issues be fully resolved prior to finalization of this SS-SAP to ensure data generated meets its intended purposes as much as possible prior to the shipment of samples to the lab.

Response: The current scope of work defines the required analytical methods for the investigation, which is the target analyte and target compound list as defined in the QAPP. SW-846 analytical methods have been selected to achieve the lowest sensitivity for the analytes and compounds. The draft SSQAPP does identify the compounds where the standard analytical methods will not achieve the Region III screening levels for the standard method lists of target compounds. The current QAPP approach is to handle the uncertainty between the Region III screening criteria and laboratory reporting levels as part of the risk assessment (for the compounds with higher reporting levels than the screening criteria).

Comment # 9: p. QAPP table 3-1. Some of the prep methods are incorrect – i.e., designate a method designed for soils to the water. Edit for consistency with the changes proposes with sections 3.1.1 to 3.1.4.

Response: Agree. The table will be edited to add prep methods and verified for consistency with Sections 3.1.1 to 3.1.4.

Comment # 10: p. QAPP table 3-2 Suggest the use of the 25g Encore sampler as the container for the TCLP VOC sample. The corrosivity (pH) method for liquid IDW should be changed to 9040B if the waste is anticipated to be aqueous in nature. Method 9045C should be retained if it is a waste (organic-based) media.

Response: Agree. The changes will be made as requested.

Comment #11: p. QAPP tables 3-9 through 3-14.

a. Suggest updating the units for the correct matrix and ensure the RBC values represent the correct media for a comparison to GW and SW.

b. Refer to comment 8 as it pertains to the additional planning necessary to compare those highlighted compounds (showing inadequate sensitivity) with the initial list of COPCs based on the existing SI data review. Suggest method modification needs be evaluated and

discussed with appropriate laboratory POCs to optimize data generated as useful for its intended purpose.

Response: a) The erroneous units will be corrected.

b) Jacobs acknowledges the comment. (see response to comment #8). The uncertainty for the compounds that have sensitivity levels greater than the Region IX PRGs will be handled in the risk assessment.

Comment # 12: p. QAPP table 3-15.

A. The acceptance criteria noted here are oversimplified for the sake of brevity. However, the following does not represent what is presented within the EPA SW-846 methods or the Shell for Analytical Chemistry Requirements (Appendix I) of EM 200-1-3. Method 8260B ICAL is not compliant with 8260B 7.3.6.2 and Shell I.9.2.2. CCC only evaluation is not correct – must be all target analytes for ICAL. The use of the mean %RSD or mean %D requires additional documentation and constraints as noted in the last paragraphs of I.9.2.2. Suggest the adoption of footnotes or other means to ensure compliance.

b. Method 8330 must be modified slightly to detect and quantitate for PETN. The same extract is used, however, the UV wavelength for PETN detection is at 210nm, and the remainder of the nitroaromatics are monitored at 254nm as established within the method. These are not typical method options addressed within the method. Therefore these details must be addressed within the appropriate QAPP documents.

Response: a) The table will be expanded to fully list the requirements of the methods and the Shell document.

b) PETN is not currently a target analyte for this site. If the scope changes to include the need for analysis of PETN, the modifications will be added to the site specific QAPP.

Reviewer Name: Crain, Mike (Geology) - HTRW Center of Expertise

Comment # 1: Field Sampling Plan, 5.3.1, pg 5-2, 1st par – Some consideration should be given to making a couple of the piezometers permanent to permit future monitoring of shallow groundwater flow directions. The arrangement of the permanent monitoring wells parallel to the direction of groundwater flow makes sense from the standpoint of monitoring contaminant concentrations. Unfortunately, this arrangement will not allow the direction of groundwater flow to be measured. The flow direction that is measured initially in the temporary piezometers may change with seasonal fluctuations in groundwater levels. If the piezometers to the west and northeast were made permanent, that would provide an adequate network of measurement points to monitor changes in groundwater flow.

Response: The temporary piezometers are to be used solely for collecting preliminary water level information to determine the feasibility of installing permanent overburden wells. Any additional use of the piezometers will discussed with the OEPA.

Reviewer Name: Charles G. Coyle (Env Engineer) – HTRW Center of Expertise

Comment # 1: p. 3-3, 3.2.4 It is noted that the text indicates that naturally occurring oil is present in the Delaware Limestone. This could represent a potential sink for partitioning and immobilization of organic contaminants in groundwater.

Response: The comment is acknowleged. This information will be retained for site evaluations during the investigation reporting.

Comment # 2: p. 5-3, 5.4 This section indicates that soil boring samples will be collected from the surface and vadose zone locations. However some soil boring samples should also be collected from locations in the saturated zone, as explained below. This section or the section on installation of monitoring well installation (5.3.1) should be revised to require that some soil boring samples be collected. Data on TOC levels (in groundwater, soil from the aquifer matrix, and also from sediments), will be important from a natural attenuation perspective (especially with regard to adsorption and irreversible binding of nitroaromatics, see Haderlein, S.B., Schwarzenbach, R.P; Environmental Processes Influencing the Rate of Abiotic Reduction of Nitroaromatic Compounds in the Subsurface. In: «Biodegradation of Nitroaromatic Compounds», J.C. Spain (Ed.). Plenum Press, New York 1995, pp.199-225. [1993). Recommend revising to to require that some soil boring samples be collected from vadose zone locations that have been impacted by nitroaromatics.

Response: The comment is acknowledged. The SOW and budget is based on a maximum of 45 soil samples, which have been judicially selected to provide the greatest amount of site characterization. These additional samples could be evaluated for later investigations following the performance of the site risk assessment.

RE: NASA Plum Brook Station
Erie County

April 29, 2004

United States Army Corps of Engineers
Nashville District
Attn: CELRN-EP-R-M (Ms. Linda Ingram)
Estes Kefauver Federal Building
801 Broadway
Nashville, Tennessee 37202-1070

Dear Ms. Ingram:

Please find below the response to comments for the commentary of the Ohio Environmental Protection Agency (Ohio EPA) with respect to the Site-Specific Sampling and Analysis Plan (SAP), Remedial Investigation, Part 1 at Reservoir No.2. Burning Ground, Former Plum Brook Ordnance Works as well as the corresponding Site-Specific Quality Assurance Project Plan (QAPP).

1. General Comment
The SAP references the use of site-specific background samples; however, it does not distinguish whether said background data is specific to the No. 2 Burning Grounds or indicative of the data obtained from the Site-Wide Background study. Please note that the collection and use of site-specific background information should be discussed in this SAP. Site-specific background can be used in addition to the United States Environmental Protection Agency (USEPA), Region IX Preliminary Remediation Goals (PRGs) when screening site data for naturally occurring inorganic compounds. If Site-Wide Background Data is available, please provide a table that summarizes the values used to represent background.

Response: No site-specific background characterization was intended. This investigation will utilize the previously established values from the Site-Wide Background Study. Further clarification will be included in the text.

2. SAP Section 3.2.2
The text discussing the extent of soil contamination should be revised to indicate that "extent" will be defined when contamination levels are below risk based concentrations or background, whichever value is lower.

Response: Delineation of site contaminants will follow the approach used at the TNT Areas A,B, and C. At the conclusion of this investigation, additional sampling will be determined and negotiated based on the initial findings. The objective of this initial investigation is not to fully and accurately define the extent of contamination exceeding RBCs. The third bullet in Section 3.2.3 will be revised to read "Further define the lateral and vertical extent of soil contamination".

3. SAP Section 3.2.2
This section should be revised to state that soil contamination exceeding USEPA Region IX "PRGs" not "RBCs" is present at the No. 2 Burning Grounds.

Response: The 1996 Site Investigation Report for the site used risk-based screening criteria based on EPA Region III tables, 1996. This statement is simply defining the results of the prior investigation and should not be changed.

4. SAP Section 3.2.4
The Site-Specific SAP states that ground water analytical data will be evaluated against background values and USEPA Region III Tap Water or residential risk-based concentrations (RBCs). Background ground water values will be provided in a final version of the Site Specific SAP when they become available. Ohio EPA is not amenable to the above approach of standards comparison. Ohio EPA recommends the use of USEPA Region IX PRGs as the primary source of risk based screening values. The Site-Wide SAP, which details general investigatory methodologies and/or protocols, states that ground water analytical data will also be compared to USEPA drinking water maximum contaminant levels (MCLs). In general, MCLs are "Applicable or Relevant and Appropriate Requirements" (ARARs) and, as such, are not considered appropriate as risk based values for the screening of constituents of concerns in ground water. Therefore, if background values are not available for comparative purposes upon initiation of Part I of the remedial investigation (RI) at Reservoir No.2. Burning Ground, USEPA Region IX PRGs should be used.

Response: Screening criteria for groundwater will be revised to reflect the use of Region IX PRGs. Site-Wide background values for groundwater should be established and ready for comparison purposes during preparation of the investigation report.

5. SAP Section 5.3.1
The remedial investigation proposes the installation of five temporary overburden piezometers around the periphery of the Reservoir No.2. Burning Ground, in part, to determine shallow ground water flow . The SAP states that the piezometers shall be constructed such that no annular materials will be utilized and a bentonite surface plug will be installed to reduce surface water infiltration. This section should be revised to specify whether the annular space will consist of in-situ (natural formation) material or some other material. Please note that precautions should be undertaken to ensure that the bentonite pellets will not reach the screened interval of the well.

Response: This section will be revised to clarify that no annular material will be introduced other than bentonite pellets for the surface seal. Additional procedures will be included to ensure that the bentonite pellets are contained at the upper 18" of the annulus and do not impact the well screen.

6. With respect to the installation of three nests of overburden and bedrock monitoring wells,

this section should be revised to note the material and dimensions of the shallow and deep monitoring wells (i.e., 2-inch, PVC, 4-inch stainless steel, etc.).

Response: The section will be revised to include the requested information.

7. The section should be revised to reference the Site-Wide SAP for the development and sampling of the proposed piezometers and monitoring wells at Reservoir No.2. Burning Ground.

Response: The last sentence in Section 5.3.1 references the development procedures established in the SWSAP for permanent monitoring wells . The temporary piezometers are to be used solely for collecting preliminary water level information to determine the feasibility of installing permanent overburden wells. Any additional use of the piezometers will discussed with the OEPA.

8. As general reminder, the contracted laboratory must be able to achieve practical quantification limits (PQLs) or method detection limits (MDLs) which provide the lowest limit of detection for the corresponding analytical method as specified in USEPA SW-846 Methods and that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The PQLs or MDLs must be lower than the corresponding maximum contaminant levels (MCLs).

Response: The laboratory MDLs are required to be determined per 40 CFR, Part 136, Appendix B or an equivalent statistical approach. The laboratory MRLs are required to be set at the laboratory MQL (or PQL) for this project to achieve as many of the project's risk based criteria as possible. In addition the analytical subcontractors are also reporting detected concentrations of target analytes down to their MDL values qualified as estimated "J".

9. SAP Section 5.3.2
The text indicates that water level monitoring will be conducted on all permanent wells on a quarterly basis prior to sampling activities. Ohio EPA is unclear as to what 'quarterly' means as well as which permanent wells will be measured. Typically, Ohio EPA interprets 'on a quarterly basis' as four events per year. Clarification should be provided as to whether only the newly installed permanent wells will be checked or all overburden and bedrock monitoring wells will be checked.

Response: Clarification will be provided to indicate that only the newly installed permanent wells at the 2BG site will be monitored. Clarification will be given as to the use of "quarterly", which refers to every three months or four times per year.

10. SAP Section 5.3.3
Clarification should be provided regarding the following sampling strategy: "samples will be collected quarterly for a minimum of two rounds". As previously noted, Ohio EPA typically associates "quarterly" with four discrete events. This section of the SAP as well as the Site-Specific Quality Assurance Project Plan should be revised incorporating the appropriate clarification.

Response: Funds are available for the collection of two rounds of data. Additional rounds will be funded at a later date and the number of rounds needed will be discussed with OEPA.

11. SAP Section 5.3.4
The SAP states that slug testing will be performed on all permanent monitoring wells. This section should be revised to state that all newly installed shallow and bedrock monitoring wells at the Reservoir No.2. Burning Ground will be slug tested to eliminate any ambiguity.

Response: The text will be revised to specify that the permanent wells include three shallow overburden and three bedrock monitoring wells. Slug testing will not be performed on temporary piezometers.

12. SAP Section 5.4
Sampling depths for surface soil should be consistent with the exposure intervals that will be defined and evaluated in the Risk Assessment. Surface soil is typically defined as the interval between 0 and 1 foot or 0 and 2 feet. Please note that "defining" the surface soil interval in this manner is consistent with the approach used in previous risk assessments associated with the former Plum Brook Ordinance Works. Under the residential exposure scenario, the subsurface soils interval may extend to a depth of 13 feet. This section should be revised to ensure that sampling intervals are consistent with previous investigations and clearly identify what depth interval is considered surface soil as opposed to subsurface soil.

Response: The text will be revised to expand the surface soil interval to include 0 to 12 inches bgs. Jacobs will remove the text regarding ten feet being the lower limit for exposure scenarios. The deep sampling interval will remain as stated, either the two foot interval above the water table or the 8 to 10 foot interval. This approach will be consistent with prior investigations at the site.

13. Since polychlorinated byphenols (PCBs) are considered a potential contaminant of concern, dioxins/furans should also be incorporated into the list of analytes for the laboratory to evaluate.

Response: Dioxins/furans are called out in the text and are associated with all trench samples, all surface soil samples inside the burn pit boundary, and the subsurface samples from 3 to 5 feet within the burn pit boundary. Funds are available for collecting 15 samples for dioxin/furan analysis. Additional sampling as needed will be evaluated at the conclusion of this investigation.

14. QAPP Section 3.1.3
The Site-Specific QAPP states that dissolved metals samples will only be collected during the initial round of ground water sampling at the six new monitoring wells at Reservoir No.2. Burning Ground. These samples will be shipped to the laboratory unpreserved and unfiltered where the laboratory will perform these activities. It is the position of Ohio EPA that ground water samples collected for dissolved metals analyses should be preserved and filtered in the field. Ground water may undergo immediate changes upon extraction from the monitoring

well. By requesting filtering from the laboratory, the sample has potentially several hours of residence time where the chemistry of the sample can vary thus rendering it unrepresentative of actual aquifer conditions. Dissolved metals ground water samples should be field filtered with a 0.45 micron inline filter.

Response: Agreed. Jacobs will amend this section of the QAPP to include field filtration of the dissolved metals samples.

15. Clarification should be provided regarding the following sampling strategy: "samples will be collected quarterly for a minimum of two rounds". As previously noted, Ohio EPA typically associates "quarterly" with four discrete events. This section of the SAP as well as the Site-Specific Quality Assurance Project Plan should be revised incorporating the appropriate clarification.

Response: Currently only two quarterly groundwater sampling events are scoped at a duration of three months apart. Additional rounds will be funded at a later date and the number of rounds needed will be discussed with OEPA.

16. The Site-Specific SAP should provide for the generation of separate piezometer, shallow (overburden), and bedrock potentiometric surface maps. Ground water surface elevations collected from piezometers and shallow (overburden) monitoring wells should not be combined into one map due to their differences in construction, installation, and development.

Response: The temporary piezometers are to be used solely for collecting preliminary water level information to determine the feasibility of installing permanent overburden wells. Any additional use of the piezometers will discussed with the OEPA.