QUALITY ASSURANCE PROJECT PLAN
Long-Term Response Action

Penta Wood Products
Town of Daniels, Wisconsin
WA No. 101-RALR-05WE/Contract No. 68-W6-0025

April 2001

QUALITY ASSURANCE PROJECT PLAN (QAPP)
Remedial Action
Penta Wood Products
Town of Daniels, Wisconsin
WA No. 101-RALR-05WE / Contract 68-W6-0025

Prepared by: CH2M HILL

Date: April 2001

Approved by:

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Tony Rutter

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CH2M HILL Site Manager
Regina Bayer

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CH2M HILL Quality Assurance Manager
Lauri Gorton

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PEL Laboratory Quality Assurance Manager

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Distribution List
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Acronyms

ACZA	Ammonia, Copper II oxide, Arsenate, and Zinc
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
CAMU	Corrective Action Management Unit
CFR	Code of Federal Regulations
COC	Chain-of-Custody
CLP	Contract Laboratory Program
CPT/IF	Cone Penetrometer Testing/Induced Fluorescence
DMP	Data Management Plan
DO	Dissolved Oxygen
DQOs	Data Quality Objectives
DRO	Diesel Range Organics
EDD	Electronic Data Deliverable
ERB	Emergency Response Branch
ERT	Emergency Response Team
EW	Extraction Well
FB	Field Blank
FTL	Field Team Leader
GAC	Granular Activated Carbon
LIMS	Laboratory Information Management System
LNAPL	Light Non-aqueous Phase Liquid
LOQ	Limit of Quantification
LTRA	Long-Term Response Action
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MW	Monitoring Well
NIST	National Institute of Standards and Technology
OSWER	Office Of Solid Waste and Emergency Response
OVA	Organic Vapor Monitor
PAL	Preventive Action Limit
PARCC	Precision, Accuracy, Representativeness, Completeness, Comparability
PCP	Pentachlorophenol
PID	Photoionization Detector
ppb	parts per billion
ppm	parts per million
PRG	Preliminary Remediation Goal
PWP	Penta Wood Products
QAM	Quality Assurance Manual
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
RFP	Response for Proposal
RPD	Relative Percent Difference
ROD	Record of Decision
RW	Residential Well

SACM	Superfund Accelerated Cleanup Model
SAS	Special Analytical Service
SDG	Sample Delivery Group
SOP	Standard Operating Procedure
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons
USEPA	United States Environmental Protection Agency
WAM	Work Assignment Manager
WDNR	Wisconsin Department of Natural Resources
XRF	X-ray fluorescence

SECTION 1

Project Management

1.1 Introduction

The United States Environmental Protection Agency (USEPA) requires that environmental monitoring and measurement efforts mandated or supported by USEPA participate in a centrally managed Quality Assurance Project Plan (QAPP). Parties generating data under this program must implement procedures so that the precision, accuracy, representativeness, completeness, and comparability (PARCC) of their data are known and documented. To meet this objective, each party must prepare a written QAPP covering each project to be performed. All participants in the project, including subcontractors, will follow the procedures and protocols in this document.

This QAPP presents the organization, objectives, functional activities and specific quality assurance (QA) and quality control (QC) activities for the Long-Term Remedial Action (LTRA) operation and maintenance work being conducted at the Penta Wood Products (PWP) site near Siren, Wisconsin.

This section provides an overall approach to managing the project, including:

- Project Organization, roles, and responsibilities
- Project definition and background
- Project task description
- Data quality objectives (DQOs)
- Special training requirements
- Documentation and records management

1.2 Project Organization

At the direction of the USEPA Region 5, CH2M HILL is responsible for all phases of the LTRA activities at the PWP site in the Town of Daniels, Wisconsin. CH2M HILL will perform the operation and maintenance of the bioventing/groundwater treatment system installed at the PWP site as well as conduct performance monitoring and residential well sampling. CH2M HILL will also provide project management. The various QA and management responsibilities of key project personnel are defined below and shown in Figure 1-1.

1.2.1 USEPA Region 5 Work Assignment Manager

The USEPA work assignment manager (WAM) has the overall responsibility for all phases of the LTRA during the first 10 years of operation. The WAM is also responsible for the review and approval of this QAPP. Tony Rutter is the WAM for the PWP site.

Insert Figure 1-1

1.2.2 WDNR Site Manager

The Wisconsin Department of Natural Resources (WDNR) site manager (SM) assigned to the PWP site is Tom Kendzierski. Mr. Kendzierski has participated in investigative, design, remedial action, and LTRA activities. The WDNR will assume full responsibility for the site after the first 10 years of operation.

1.2.3 CH2M HILL Program Manager

The CH2M HILL program manager is Ike Johnson. He has overall responsibility for meeting USEPA objectives and CH2M HILL quality standards. In addition, the program manager is responsible for technical QC and project oversight.

1.2.4 CH2M HILL QA Manager

The QA manager is Lauri Gorton. The QA manager will remain independent of direct job involvement and day-to-day operations and has direct access to management staff to resolve QA disputes, as necessary. Specific functions and duties include the following:

- Directing the QA review of the various phases of the project, as necessary
- Directing the review of QA plans and procedures
- Providing QA technical assistance to project staff, as necessary

1.2.5 CH2M HILL Site Manager

The CH2M HILL site manager is Regina Bayer. The SM is responsible for implementing the project and is authorized to commit resources to meet project objectives and requirements. The SM's primary function is to achieve technical, financial, and scheduling objectives. The SM will report directly to the USEPA Region 5 WAM and will be the major point of contact for matters concerning the project. More specifically, the SM will:

- Define project objectives and develop a detailed work plan and schedule
- Establish project policy and procedures to address specific needs of the project as a whole, as well as the objectives of each task
- Acquire and apply technical and corporate resources to meet budget and schedule constraints
- Orient field leaders and support staff with regard to the project's special considerations
- Monitor and direct other team members
- Develop and meet ongoing project or task staffing requirements, including mechanisms to review and evaluate each task product
- Review the work performed on each task to ensure quality, responsiveness, and timeliness
- Review and analyze overall task performance with regard to planned schedule and budget
- Review external reports (deliverables) before submission to USEPA Region 5
- Represent the project team at meetings and public hearings

1.2.6 CH2M HILL Review Team Leader

The review team leader is Phil Smith. The role of the review team leader is to support the SM in site management activities and to coordinate CH2M HILL internal reviews. The review team leader will also be involved in ongoing planning activities.

1.2.7 CH2M HILL Project Chemist

The CH2M HILL project chemist is Paul Arps. He will be responsible for tracking data and overseeing the data evaluation. Specific responsibilities include the following:

- Schedule the analytical laboratories
- Oversee the tracking of samples and data from the time of field collection until results are entered into a database
- Coordinate activities with laboratories and data validators
- Oversee data validation and production of result tables
- Evaluate data usability

1.2.8 CH2M HILL Treatment Plant Manager

The CH2M HILL treatment plant manager is Bill Andrae. He will be responsible for overseeing the operation and maintenance of the biovent/water treatment plant. Specific responsibilities include the following:

- Day-to-day communications with the plant operator
- Monitoring the performance of the plant and initiating corrective actions or modifications as needed
- Performing routine reporting of system operations and performance results

1.2.9 CH2M HILL Treatment Plant Operator

The CH2M HILL treatment plant operator is Mary Wicklund. She will be responsible for the day-to-day operations of the facility. Specific responsibilities include the following:

- Collecting effluent and influent samples at the frequency consistent with the WPDES permit.
- Performing routine inspection and maintenance of the facility and the PWP site
- Performing troubleshooting as directed by the plant manager

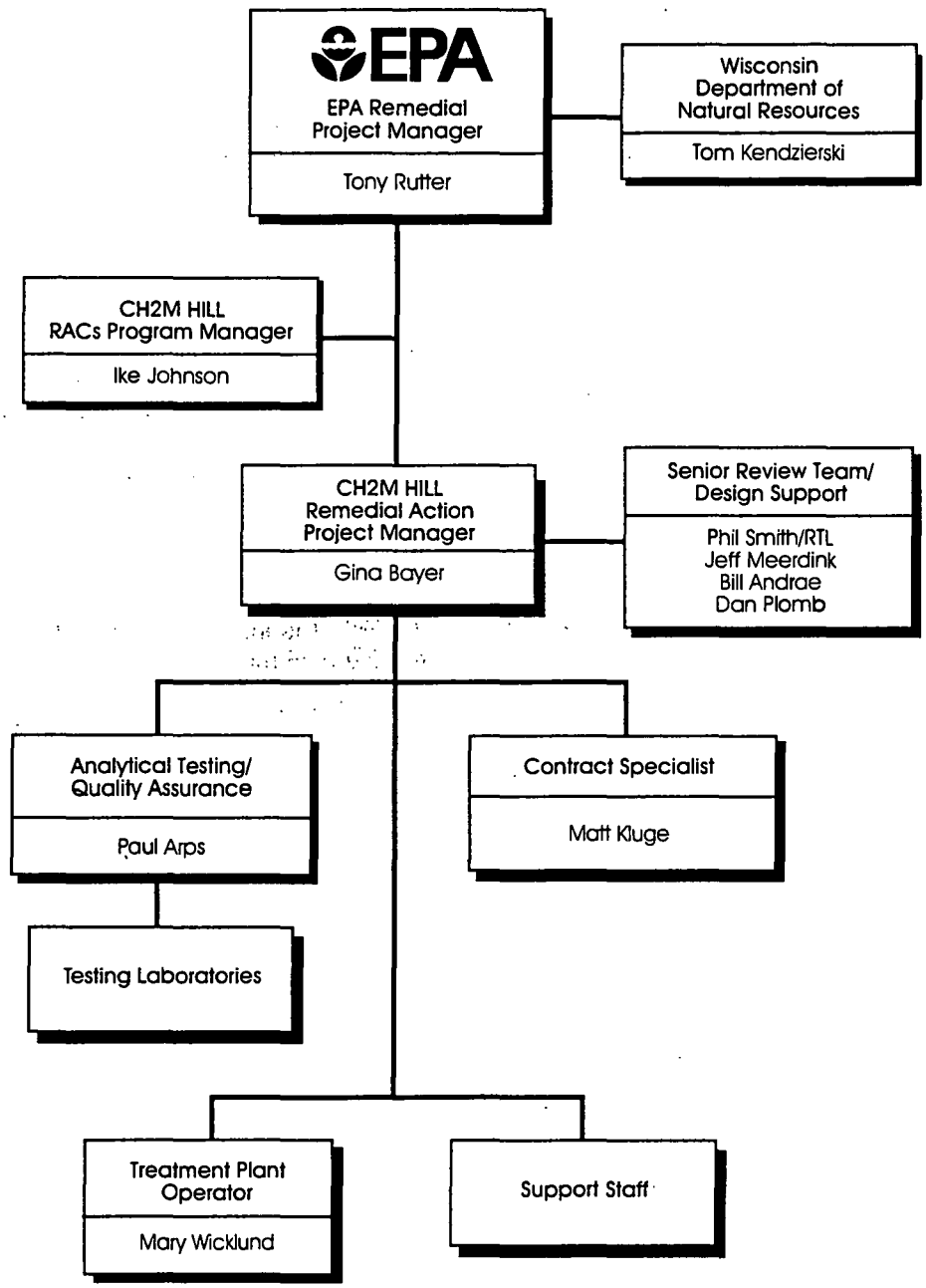

FIGURE 1-1
Team Organization
Penta Wood Products Site
Quality Assurance Project Plan

1.3 Problem Definition/Background Information

1.3.1 Penta Wood Products Operations/Early Investigations

From 1953 to 1992, PWP operated on 80 acres of a 120-acre parcel 2 miles west of Siren, Wisconsin (Figure 1-2). Raw timber was cut into posts and telephone poles and treated with either a 5- to 7-percent pentachlorophenol (PCP) solution in a No. 2 fuel oil carrier or with chemonite, a water-borne salt treatment consisting of ammonia, copper II oxide, arsenate, and zinc (ACZA). During its 39 years of operation, PWP discharged wastewater from an oil/water separator down a gully to a lagoon on the northeast corner of the property. Figure 1-3 shows site features and topography that existed in 1997 before the Remedial Action was conducted, and shows the PCP groundwater plume caused by these discharges, as measured in 1994, 1997, and 2000.

Process wastes were also discharged onto the wood chip pile in the northwestern portion of the property. WDNR investigators noted several large spills, stained soils, and poor operating practices in 1986. A 6-acre portion of the site, located south of old Highway 70, was used to transfer bulk PCP/oil mix to buyers.

In 1988, the onsite production well was closed for potable use when it was found to contain 2,700 parts per billion (ppb) of PCP. From 1989 to 1992, PWP funded an investigation to characterize soil and groundwater contamination with 58 soil borings, test pits, and 10 monitoring wells.

The PWP facility was closed in May 1992 because it could not comply with Resource Conservation and Recovery Act regulations. In 1993, the WDNR conducted a Screening Site Inspection that detected 13 ppm PCP, 190 ppm copper, and 74 ppm of arsenic in a sediment sample collected from a wetland located downhill from the lagoon. Five residential wells were sampled and did not contain site contaminants.

Surficial soils and ash from the boiler where PCP sludges were burned were sampled at various times for dioxin. Sample results detected dioxin at less than 1 μg/kg toxicity equivalent using the 1987 USEPA toxicity equivalency factors.

1.3.2 Emergency Removal Action and Investigation

The State of Wisconsin selected PWP as a Superfund Accelerated Cleanup Model (SACM) site in 1994. A federally funded removal action was conducted between April 1994 and June 1996 by USEPA Region 5 Emergency Response Branch (ERB). About 28 storage tanks containing liquids and sludges were emptied, and 43,000 gallons of PCP/oil and sludge were disposed of offsite for incineration. The ACZA treatment building was demolished, and the grossly contaminated soils from that area were excavated. About 1,600 cubic yards of contaminated soils (PCP and arsenic) were excavated from the site and hauled offsite. About 4,000 cubic yards of ACZA-contaminated soil was excavated and mixed with concrete onsite to form a 580- by 260-foot, 1-foot-thick concrete pad. The pad was intended to be used for ex situ bioremediation of PCP-contaminated soils.

NORTH

0 1

SCALE IN MILES

FIGURE 1-2
Site Location Map
Penta Wood Products RA Construction QAPP

CH2MHILL

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NOTES:

1. DASHED CONTOUR LINES LOCATED IN THE NORTHEAST WETLAND AREA HAVE BEEN ADJUSTED TO CONFORM WITH SURVEYED LOCATIONS OF SEDIMENT SAMPLES AND THE DESCRIPTIONS PROVIDED BY THE SURVEYORS. THE CONTOURS MAY NOT REFLECT ACTUAL TOPOGRAPHY IN THIS AREA.
2. DASHED CONTOUR LINES LOCATED IN THE CENTRAL SITE AREA REPRESENT THE TOPOGRAPHIC SURVEY PERFORMED BY SALO ENGINEERING, INC. ON OCTOBER 29, 1997 FOR CH2M HILL, INC.

LEGEND

- LYSIMETER LOCATION
- INFILTRATION TEST BORING LOCATION
- UNCONFINED MONITORING WELL LOCATION
- SEMICONFINED MONITORING WELL LOCATION
- GROUNDWATER GRAB LOCATION
- WELL OR BORING WITH LNAPL
- DECREASE/STABLE PCP
- INCREASE IN PCP
- WASTEWATER LAGOON
- BOUNDARY OF WOOD CHIP PILE

3.5 / 0.7J / 0.6 — PCP CONCENTRATION (ug/L) 1994 / 1997 / 2000

- BOUNDARY OF LNAPL
- 1994 ND — 1994 PCP NON-DETECT CONTOUR
- 1997 ND — 1997 PCP NON-DETECT CONTOUR
- 2000 ND — 2000 PCP NON-DETECT CONTOUR

NOTE:
1. MCL/WDNR ES FOR PCP IS 1.0 ug/L.

N

0 100' 200'

N 2200 N 2000 N 1800 N 1600 N 1400 N 1200 N 1000 N 800 N 600 N 400

E -200 E 0 E 200 E 400 E 600 E 800 E 1000 E 1200 E 1400 E 1600 E 1800 E 2000 E 2200 E 2400 E 2600

MW 11: 1.0 / 1.0U / 0.6U
MW 8: 4.3 / 1.0U / 0.5U
MW 17: 2,000 / 1.0U / 5 / 0.5U
4
GW01: 6.2
MW 7: 0.4 / 1.0U / 0.5U
1.0U
MW 9: 1.2 / 1.0U / 0.6
1.0U
GW 06: 3.2
MW 13: 3.5 / 0.7J / 0.8
GW 05: 4.3
GW 04: 1.4
2000 ND
GW02: 9.4
MW 5: 26,000 / 28,000 / 29,600
MW 2: 0.7 / 1.0U / 0.5U
GW03/ PZ 01: 1.0U
MW 16: 0.3 / 1.0U / 0.5U
MW 12: 10,000 / 13,000 / 10,600
17,000 / 8,200 / 9,530
MW 10
MW 10S
MW 18: 3,300 / 27,000
110,000 / 30,000 / 56,100
BIOVENTING/ EXTRACTION WELL EW 4
MW 6S: 7.3 / 1.0U / DRY
MW 20
3,900 / 29,000
MW 14: 2.3 / 1.0U / 0.5U
MW 19: 53,300 / 19,000 / 11,000
MW 1: 0.3 / 2.1 / 0.5U
MW 6: 4,300
MW 4: 1.9 / 1.0U / 0.5U
1.0U
PW 01: 140 / 5.0
-2000 ND
1997 ND
1994 ND
1.0U
1.0U
DANIELS 70
MW 3: 2.6 / 1.0U / 0.6U
MW 15: 1.3 / 1.0U / 0.5U

0.9J / 2.0 / 1.0U

FIGURE 1-3
1994, 1997, AND 2000 PCP CONCENTRATIONS IN GROUNDWATER
APRIL 2000 SAMPLING EVENT
PENTA WOOD PRODUCTS RA REPORT

CH2MHILL

In June 1995, a heavy rain released water from the lagoon into the wetlands northeast of the site. The removal team responded by building a retention pond adjacent to the lagoon and stockpiling excavated soil across gullies to reduce soil erosion.

During the removal action, ERB requested removal assistance and site characterization support by the USEPA Emergency Response Team (ERT). In 1994, an ERT conducted a hydrogeological and an on and offsite surficial soil investigation. The hydrogeological investigation included installation of 12 additional wells, three lysimeter nests, infiltration tests, and seismic studies (ERT, 1994). About 300 soil samples were collected during soil boring installation and analyzed for PCP, total petroleum hydrocarbons (TPH), arsenic, copper, and zinc.

The soil investigation consisted of establishing a 200-foot interval grid system over the entire site and northeast of the property boundary. Soils were collected at 1-foot intervals down to 5 feet and analyzed with immunoassay kits for PCP and field portable X-ray fluorescence (XRF) for arsenic. The ERT conducted laboratory treatability studies, including soil washing and stabilization/solidification; and pilot-sized bioremediation treatability studies including land farming, ex situ biopiles, anaerobic dechlorination, and white rot fungus. Contaminated groundwater and wash water were treated with a Biotrol fixed-film biological reactor. The ERT did not complete all of its intended activities because of cut-backs in federal funding in 1995.

1.3.3 Remedial Program Activities

1.3.3.1 RI/FS

The site was placed in the USEPA remedial program in 1996. CH2M HILL conducted Remedial Investigation/Feasibility Study (RI/FS) field activities for the USEPA in October 1997 to fill data gaps remaining after a site characterization investigation performed by ERT in 1994 and a removal action conducted by ERB in 1994 and 1996. RI activities included groundwater and residential well sampling, surface water and sediment sampling, surficial soil sampling, a subsurface soil investigation consisting of cone penetrometer testing/induced fluorescence (CPT/IF) and test pit excavation, and a screening level ecological investigation. In January through February 1998, five new monitoring wells were installed and sampled, along with an extraction/bioventing well and nine soil gas wells for a bioventing treatability study.

1.3.3.2 ROD

The culmination of the RI/FS was the Record of Decision (ROD) signed in September 1998. The selected remedy consists of soil and sediment consolidation, light non-aqueous phase liquid layer (LNAPL) collection and disposal, groundwater collection and treatment associated with the LNAPL collection, bioventing, and monitored natural attenuation for the remainder of the groundwater plume. The remedy focuses on removing free phase LNAPL and the grossly contaminated groundwater (above 1,000 µg/L PCP) while drawing down the water table and enhancing natural biodegradation of the PCP/oil-contaminated soils above the LNAPL zone by bioventing (adding air to the vadose-zone soils and exposed smear zone).

The selected remedy removes the contaminants from the natural environment in the following manner:

- Free-phase LNAPL is extracted from the water table and incinerated offsite.

- Extracted ground water is treated with carbon and discharged onsite into an infiltration basin to percolate through 100 feet of clean sand to the water table.
- Bioventing of the exposed smear zone will enhance natural degradation of residual LNAPL, and bioventing of the vadose soils will enhance biodegradation of PCP/oil contamination. It is estimated that 80 to 90 percent of the estimated 120,000 pounds of PCP will be reduced in 10 years of bioventing system operation.
- Natural attenuation is also occurring in the aerobic portion of the ground water plume, reducing PCP to chloride, carbon dioxide, and water.
- Arsenic-contaminated soils will be solidified to prevent migration, and placed under a cover to prevent direct contact.

1.3.3.3 Remedial Design

Additional site studies were conducted during pre-design from May 10 to May 26, 1999, including soil sampling for total and leachable arsenic, conducting groundwater pump tests, sampling influent and effluent water from a granular activated carbon (GAC) treatment system for the pump test water, and other miscellaneous sampling for specific predesign evaluations.

1.3.3.4 Remedial Action

During the remedial action, contaminated soils were excavated and consolidated into a 7-acre Corrective Action Management Unit (CAMU), as shown in Figure 1-4. PCP-contaminated soils were deposited on the southern portion of the CAMU and arsenic-contaminated soils were placed on the northern portion of the CAMU. A wall of concrete rubble and stabilized arsenic-contaminated soil divides the two portions. The CAMU is covered with 6 inches of sand followed by 6 inches of topsoil.

Remedial construction activities in support of the remedial action began in January 2000 and included the demolition of 17 buildings and foundations, and the offsite disposal of demolition material, debris piles, and laboratory chemicals. Soils were stabilized and consolidated, pipes were laid, and manholes and an infiltration basin were installed. Drilling operations included abandonment of existing wells and the installation of the multi-purpose biovent and groundwater extraction wells, soil gas wells, a monitoring well, and the groundwater and LNAPL recovery pumps. A pre-fabricated treatment building, the groundwater treatment system, and the biovent blower system were installed. The remedial construction was completed in September 2000.

1.3.3.5 LTRA

The Long-Term Remedial Action (LTRA) will be conducted by CH2M HILL to operate and maintain the constructed remedy to meet the remediation goals specified in the ROD. The LTRA includes assessing existing groundwater contaminant concentrations, monitoring the ongoing natural attenuation process, and evaluating the bioventing treatment system. The water treatment system will be monitored to evaluate the contaminant removal effectiveness and compliance with the Substantive Requirements of a WPDES Permit (No. WI-0061531-01-0) prepared by the WDNR for the Penta Wood Site.

N 2200
N 2000
N 1800
N 1600
N 1400
N 1200
N 1000
N 800
N 600
N 400

E -400
E -200
E 0
E 200
E 400
E 600
E 800
E 1000
E 1200
E 1400
E 1600
E 1800
E 2000
E 2200
E 2400
E 2600

N

0 100 200 300
SCALE IN FEET

APPROXIMATE PROPERTY BOUNDARY

CAMU BOUNDARY

INFILTRATION BASIN AND LEACH FIELD

EFFLUENT DISCHARGE LINE

TREATMENT BUILDING

MW 8
MW 11
MW 17
MW 13
MW 16
MW 12
MW 9
MW23
MW 2
MW 5
MW 18
MW 10
MW10S
MW 14
MW 1
MW 4
MW19
MW20
MW06S
MW 6
MW 7
MW24
MW25
MW22
MW21
MW 3
LY 1
LY 2
LY 3
EW-01

MW-26
N 1682.23
E 599.17

WELL NEST 02
N 1300.71
E 1399.65

WELL NEST 03
N 1169.67
E 1300.48

WELL NEST 10
N 1082.06
E 1387.28

WELL NEST 04
N 1015.75
E 1188.29

WELL NEST 11
N 1567.53
E 1679.22

SOIL GAS WELL NEST 04
N 1257.63
E 1460.36

WELL NEST 05
N 1159.90
E 1569.75

SOIL GAS WELL NEST 05
N 1074.92
E 1510.58

WELL NEST 06
N 1011.23
E 1480.39

SOIL GAS WELL NEST 06
N 891.59
E 1487.57

WELL NEST 07
N 860.22
E 1370.30

SOIL GAS WELL NEST 07
N 917.80
E 1222.85

BIOVENTING WELL 08
N 830.11
E 1090.06

BIOVENTING WELL 09
N 760.03
E 879.67

SOIL GAS WELL 22
N 799.96
E 997.68

1097
1093.0
1092.0
1091.0
1090.0

TARGET GROUNDWATER COLLECTION AREA

TARGET LNAPL RECOVERY AREA

TARGET BIOVENTING AREA

1997 PCP NON-DETECT CONTOUR

Figure 1-4
CAMU, Well, and Soil Gas Nest Locations

CH2MHILL

HERCULES/PROJ/EPA/151745-PENTAWOOD/CAD/DRAWINGS/CONSTDOCS/QAPPFIG2-2.dgn

1.4 Project Description and Schedule

1.4.1 Project Description

The sampling events that will take place during the LTRA include assessing groundwater contaminant and natural attenuation parameter concentrations, monitoring compliance with WPDES permit requirements for the treatment plant, and collecting soil and soil gas samples to monitor oxygen uptake and contaminant reduction in soil resulting from the bioventing system operation.

Groundwater contaminant and natural attenuation parameter concentrations will be assessed by the collection of monitoring well and residential well samples. The treatment system's influent and effluent contaminant concentrations will be monitored to assess compliance to the effluent limits specified in the Substantive Requirements of a WPDES Permit.

The bioventing system will be initiated once the LNAPL plume in the groundwater table is removed. The effectiveness of the bioventing will be evaluated after 5 years based on analytical results collected from the groundwater and soil environmental monitoring. However, soil and soil gas samples will be collected during operation to monitor the performance of the bioventing system.

1.4.2 Project Schedule

Monitoring well, extraction well, residential well, treatment system sampling, and soil sampling will be conducted by CH2M HILL and is currently under contract to be conducted through September 2003. The sampling schedule is described in detail in Section 2 of this QAPP.

1.5 Data Quality Objectives and Criteria for Measurement Data

DQOs are qualitative and quantitative statements that specify the quality of data required to support decisions made during or after site-related activities. Project specific DQOs are developed with the seven-step process presented below.

1.5.1 Step 1: State the Problem

As a results of spills and past waste handling practices at the site, subsurface soils to a depth of over 100 feet are contaminated with a PCP/oil mixture beneath the gully where wastewater was discharged from an oil/water separator to a lagoon. Over the years, PWP filled erosion gullies with wood debris. This wood debris layer became semi-saturated with PCP/oil mixture. The PCP/oil mixture, which has traveled to the groundwater and spread horizontally as a LNAPL layer, is in equilibrium with pore pressures and is not expected to continue spreading. A LNAPL layer of PCP/oil is floating on the water table over an estimated 4-acre area.

A dissolved-phase PCP plume exists in the groundwater and appears to be stable. PCP concentrations in groundwater have been monitored at the site since 1988, and some of the wells have 12 rounds of sampling data. PCP groundwater concentrations have shown consistent declines at the majority of the monitoring wells over time. There is a general

decrease in the size of the PCP plume, as can be seen in Figure 1-3 that shows the plume size in 1994, 1997, and 2000. There is no evidence of contaminated groundwater discharging to the wetland or migrating below the wetland to surface water bodies.

Additional evidence that PCP is biodegrading in groundwater is supported by the natural attenuation parameter data. The groundwater is under anaerobic conditions in both the unconfined and semi-confined aquifer in the LNAPL plume area. The anaerobic plume is not expanding, which is important because aerobic biodegradation has a faster decay rate than anaerobic biodegradation; therefore, biodegradation should be capable of preventing the further expansion of the plume.

PCP contaminated soils are still present in the CAMU located at the site. The PCP contamination in the CAMU is at the highest levels at the "smear zone," the subsurface soil interval that is in contact with the LNAPL. The biovent system will be activated once the recoverable LNAPL layer has been removed from the aquifer, so the positive air pressure does not spread the LNAPL.

1.5.2 Step 2: Identify the Decision

The objectives of the LTRA monitoring activities are to:

- Continue to monitor existing groundwater contaminant and natural ion parameter concentrations
- Confirm that contaminants do not extend to drinking water wells
- Provide information to assist in the operation of the groundwater treatment facility and bioventing system and monitor their performance
- Monitor compliance with WPDES Permit discharge requirements through the collection and analysis of treatment system influent and effluent samples
- Evaluate treatment system residuals and LNAPL contaminant concentrations for disposal purposes
- Sample and analyze soil gas samples to monitor oxygen uptake and contaminant reductions in soils resulting from bioventing system operation

1.5.3 Step 3: Identify the Inputs to the Decision

Monitoring well and residential well groundwater samples will be collected and analyzed to assess plume size and concentration and to verify that contaminants have not impacted drinking water wells.

Influent and effluent water treatment plant water samples will be collected and analyzed to assess discharge compliance with the WPDES-like permit. Water samples will also be collected between treatment system components as needed to evaluate system performance when problems arise in meeting effluent concentration limits.

Groundwater levels in extraction wells (EW-2 through EW-7, EW-10, and EW-11) are monitored and recorded to assess the water table drawdown during treatment system

operation. Additional groundwater levels will be collected during sampling events using a water level indicator.

LNAPL depth levels will be collected to monitor the effectiveness of the product extraction portion of the treatment system.

Soil and soil gas samples will be collected and analyzed to assess the performance of the bioventing system in further degrading the PCP concentrations in the CAMU and assessing if the soil cover and erosion control measures for the CAMU are preventing the transport of PCP.

Waste disposal characterization samples were collected from the product storage tank and spent clay and carbon by the waste disposal firm. The samples were analyzed for parameters set by the receiving disposal facility, which was approved by the USEPA as in compliance with all appropriate regulations. The disposal facilities are outside the state of Wisconsin as there are no disposal facilities in Wisconsin certified to accept F027 /FO32 wastes.

An offsite laboratory subcontracted by CH2M HILL will analyze the samples, with the exception of the waste disposal characterization samples. The subcontracted laboratory will use the appropriate analytical methods to reach the project specific analytical requirements. Initial waste disposal characterization samples were analyzed by Safety Kleen, the facility who initially disposed of the collected product and treatment residuals.

1.5.4 Step 4: Define the Study Boundaries

Current PWP site property boundaries enclose approximately 80 acres. The PWP property initially included 120 acres, but 40 wooded-acres that were not actively used during treatment processes were transferred to a neighboring land owner in the early 1990s. Surficial soil, sediment, and surface water contamination did extend outside the property boundaries to the northeast. The northern wall of the lagoon the wastewater was discharged to collapsed, and both PCP/oil and arsenic contamination traveled by overland transport down a steep hill and into an off-property wetland. During the Remedial Action this contamination was physically removed, and brought back onto the site property and contained in the CAMU.

The contaminants of concerns for the LTRA are contained in the onsite CAMU, or located in the aquifer directly below the site. The CAMU consists of about 7 acres (Figure 1-4). The LNAPL zone consists of about 4 acres. The groundwater plume containing PCP above the PAL limit of 0.1 µg/L is about 14 acres (Figure 1-3), and has been shrinking over time, based on 1994, 1997, and 2000 groundwater data.

Various residential wells located to the southwest, south, southeast, east, northeast, and north of the site have been monitored for PCP, and sometimes benzene, toluene, ethylbenzene, and xylene (BTEX), at varying frequencies starting in 1993. Site contaminants have not been found in the offsite residential wells; ongoing monitoring is a precaution.

1.5.5 Step 5: Develop a Decision Rule

1.5.5.1 Groundwater

According to the ROD, which was based on the 1994 and 1997 monitoring well data, four ground water chemicals of potential concern (PCP, benzene, naphthalene, and arsenic) are present at concentrations associated with elevated risk estimates, and three chemicals of potential concerns (iron, manganese, and chloride) are present at levels above taste or odor aesthetics levels. Exposure to PCP accounts for over 99 percent of the baseline carcinogenic risk and baseline noncarcinogenic risks estimated in the Focused Human Health Risk Assessment (FHHRA). Remedial actions taken to reduce exposure to or concentration of the PCP/oil layer will result in a concurrent reduction of exposure to other compounds present in the ground water. Benzene and napthalene are associated with the fuel oil carrier, and the elevated arsenic, iron, and manganese levels are native minerals solubilized due to reducing conditions caused by the presence of the LNAPL source. Table 1-1 lists the federal MCL, risk-based, and state groundwater quality standards for these COPCs. The WDNR Preventive Action Limits (PALs) are the clean-up criteria for the ground-water at the PWP site. PCP is the main contaminant of concern with a PAL of 0.1 µg/L. The parameter list and required reporting limits (NR 140 PALs) are listed in Section 2 of this QAPP.

The clean-up criteria for the aquifer under natural aerobic conditions are anticipated to be met through natural attenuation. PCP concentrations and natural attenuation parameters will be routinely monitored. The ROD states that if monitoring detects that off-site receptors are threatened, or if the remedy fails to effectively reduce contaminant mass within a reasonable time frame (30 to 40 years), contingency plans will be implemented. Potential contingency plans include point-of-use carbon treatment for residential wells, and a more aggressive PCP/LNAPL residual zone treatment technology, such as steam injection in conjunction with soil vapor extraction.

1.5.5.2 Water Treatment System Effluent

The discharge criteria stated in the Substantive Requirements of a WPDES Permit are the clean-up criteria for the treated groundwater being discharged back to the PWP site. The WPDES permit limits are based on the PALs as stated in NR 140 Wis. Adm. Code. The parameter list and required reporting limits are listed in Section 2 of this QAPP. The WPDES permit parameter list includes more parameters than the parameters defined as chemicals of potential concern in the ROD. The additional parameters were added at the WDNR's discretion, and includes dioxins and furans, which are a byproduct or contaminant of PCP synthesis in some commercial grades of PCP. The levels of dioxins/furans detected during site investigations did not exceed established removal criteria (Remedial Investigation Report, 1998).

System monitoring samples may be collected in the event that the discharge permit requirements are not met. Corrective action may be implemented to resolve system problems associated with elevated effluent concentrations exceeding discharge criteria. Alternatively, a request to increase effluent limits may be submitted as described in Section 2.2.1.1 of the Substantive Requirements of a WPDES Permit.

TABLE 1-1
Clean Up Goals for Constituents of Potential Concern in Groundwater
Record of Decision, Penta Wood Products Site, Town of Daniels, Wisconsin

		Parameters Considered in Setting Clean up Goals for Groundwater						
		Federal MCLs		Residential Adult[a]			Wisconsin Groundwater Quality Standards	
Compound	Clean Up Goals (µg/L)	Primary MCL (µg/L)	Secondary MCL[b] (µg/L)	Cancer Risks 10^{-6} (µg/L)	Cancer Risks 10^{-4} (µg/L)	Noncancer Risks HI=1 (µg/L)	Enforcement Standard (µg/L)	Preventive Action Limit (µg/L)
Arsenic	5	50	--	0.045	4	11	50	5
Benzene	0.5	5	--	0.30	30	12.5	5	0.5
Chloride	125,000[b]	--	250,000	--	--	--	250,000[b]	125,000[b]
Copper	130	--	1,000	--	--	1,351	1,300	130
Ethylbenzene	140	700	--	--	--	1,327	700	140
Iron	150[b]	--	300	--	--	--	300[b]	150[b]
Manganese	25[b]	--	50	--	--	5,110	50[b]	25[b]
Naphthalene	8	--	--	--	--	1,460	40	8
Pentachlorophenol	0.1	1.0	--	0.56	56	1,095	1.0	0.1
Toluene	69	1,000	--	--	--	749	343	68.6
Xylene, mixture	124	10,000	--	--	--	73,000	620	124
Zinc	2,500[b]	--	5,000	--	--	10,950	5,000[b]	2,500[b]

" -- " = No criteria.
[a] PRGs for residential exposures are based on ingestion and inhaltion using U.S. EPA Region IX approach for tap water.
[b] Criteria is for public welfare concerns (taste or odor aesthetics).

1.5.5.3 Soils

The clean-up criteria for soil and sediment outside of the CAMU have been met during the RA by excavating the material and consolidating it into the CAMU. Per the ROD, PCP-contaminated material within the CAMU is considered remedied when it no longer causes groundwater contamination exceeding 0.1 µg/L PCP, the NR 140 PAL (ROD, page 41). The soil cleanup goal protective of groundwater presented in the ROD is 4.6 mg/kg. It was developed based on Sommers Model methodology (Roy F. Weston, 1994), which does not account for the relatively slow leaching rate of PCP. It also has a relatively high degree of uncertainity because of the assumptions made in the model. Although the bioventing performance standard is set at 4.6 mg/kg, it may be modified in the future if it is found that a differing value is protective of groundwater.

Leaching tests conducted on site soils during the RD determined the concentration of arsenic in soil at which the arsenic leaches to groundwater. Soils containing arsenic above that level were solidified with cement and buried within the CAMU. Soils with lower levels of arsenic were consolidated on the north end of the CAMU and covered with a foot of clean material.

The objective of the long-term performance monitoring program is to assess the degree and effectiveness of PCP removal and whether the soil cover and erosion control measures are preventing transport of arsenic and PCP. Monitoring activities for bioventing and cover maintenance will include:

- Soil gas analyses below bioventing treatment areas
- Soil sampling within bioventing treatment areas
- Routine inspection of cover and sampling if necessary

Newly installed soil gas wells allow for the monitoring of soil gas composition to assess effectiveness in delivering air to the affected subsurface regions. Soil gas analyses will be conducted annually once the bioventing system is in operation.

Soil samples for PCP, TPH, and Diesel Range Organics (DRO) will be collected one to three times during the operational period of the bioventing system. Investigation data used TPH to baseline diesel oil concentrations. DRO analysis has been added to meet Wisconsin regulations. Samples will be collected at discrete locations and at various depths. Based on the results, a decision to continue bioventing operation and/or implement another treatment alternative will be made.

1.5.6 Step 6: Specify Limits on Decision Errors

The probability of sampling and measurement errors that exist at any site under investigation necessitates the development of sampling guidelines and the collection of quality control samples. Field errors are minimized by having each member of the field team follow the same standard operating procedures (SOPs) for sampling. Sampling techniques are discussed in detail in Appendix C of this QAPP. QC samples are used to verify the accuracy and precision of the data. When a QC sample is outside of the established control limits, the data will be qualified and field corrective action will be implemented when applicable (e.g., field duplicates are outside established control limits).

Field collected data such as groundwater pH, temperature, conductance, DO, redox will not be subject to data validation procedures. Similarly, soil gas data and treatment plant data collected to assess the operation of the systems will not be validated or subject to stringent QC measures.

1.5.7 Step 7: Optimizing the Design

The objective of the sampling design is to assess the degree and effectiveness of LNAPL removal, groundwater treatment, monitored natural attenuation, and bioremediation through bioventing. The monitoring well sampling schedule (Section 2 of this QAPP) will create a snapshot of time as to the current groundwater contaminant concentrations and natural attenuation effectiveness at the site. A small number of monitoring wells will be monitored on a quarterly basis, while a larger set of wells will be monitored annually. Contaminant and natural attenuation parameter trends will be tracked and the sampling scheme modified as appropriate to monitor changing conditions (i.e., there is flexibility in which wells will be sampled during the quarterly events). .

A map showing electron acceptor concentrations (nitrate and sulfate) and metabolic byproduct concentrations (ferrous iron, manganese and methane), as well as oxidation-reduction potential (ORP), TOC, and dissolved oxygen (DO) are shown in Figure 6-4 for the unconfined wells, and in Figure 6-5 for the semiconfined wells in the RI Report (June 1998). Each monitoring well is also identified as to whether the groundwater is aerobic or anaerobic. During aerobic biodegradation, DO levels will decrease to levels below background, with the amount dependent on the concentration of the organic substrate and its degradability. If the organic substrate concentration (e.g., PCP or TPH) is low, DO will not be depleted and the groundwater will remain aerobic. Degradation of 1 mg/L of TPH requires about 3 mg/L oxygen and degradation of 1 mg/L PCP requires about 0.7 mg/L oxygen. Background DO is about 8 mg/L in the groundwater. Degradation of 1 mg/L PCP would be expected to produce 0.7 mg/L chloride.

Where PCP or TPH concentrations are in the mg/L range, the DO may be depleted and approach zero. The groundwater becomes anaerobic and the bacteria capable of using lower energy electron acceptors such as nitrate, manganese IV, and iron III are favored. During anaerobic degradation the concentrations of electron acceptors such as nitrate will decrease to levels below background, while concentrations of the more soluble reduced iron and manganese will increase under reducing conditions relatively insoluble naturally occurring arsenic V will be reduced, forming the more soluble arsenic III. Elevated arsenic in groundwater is present only in the anaerobic reducing portion of the plume. Refer to the 1998 RI Report for historical trends of monitoring data and an evaluation of the Penta Wood natural attenuation parameter data.

The WPDES Permit sampling schedule is found in Section 2 of this QAPP. Additional samples may be collected to troubleshoot the treatment system process if problems arise.

The number of soil and soil gas samples collected will be sufficient to characterize the effectiveness of the bioventing system at the site.

1.5.8 Measurement Performance Criteria

The measurement performance criteria are checked on several levels:

- Built-in QC standards
- Senior review
- Management controls

The measurement data must abide by specific QC standards. Data that does not meet these standards is qualified accordingly. The analytical data and the QC results are checked by the bench chemist, the Laboratory's QA Manager, CH2M HILL's project chemist, and the USEPA's data validator.

All documents which pertain to the quality standards of the project are drafted by, and reviewed internally by, CH2M HILL staff with relevant technical experience. While performing field sampling activities, the FTL will supervise activities to assess if SOPs are being followed. Specific QC checks and corrective action measures are described in Section 3 of this QAPP.

1.6 Instructions for Special Training Requirements/Certification

As noted under Section 1.2, Project Organization, project team members have been chosen with the necessary experience and technical skills to perform required project tasks.

The subcontractor chosen to perform laboratory analyses will meet project-specific requirements and the specifications of the USEPA and WDNR. At this time the contracted laboratory, PEL Laboratories, is not a Wisconsin-certified laboratory. The laboratory subcontract will be rebid in September 2001 when the subcontract period of performance is over. A criteria for the new subcontract will be that the laboratory must be Wisconsin-certified.

Project team members, including subcontractors, performing fieldwork will be required to show proof of meeting 29 CFR 1910.120 regulations.

1.7 Instructions for Documentation and Records

1.7.1 Field Sampling Documentation

Field sampling activities will be recorded in field logbooks. Field logbook entries will be described in as much detail as possible so that persons going to the site could reconstruct a particular situation without reliance on memory. Modifications to field sampling protocols must be documented in the field logbook. The FTL is responsible for ensuring that modifications to sampling protocols are so documented.

Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to the field crew, but will be stored in a secure location when not in use. Project-specific document numbers will identify each logbook. The title page of each logbook will contain the following:

- Person to whom the log book is assigned
- Logbook number
- Project name
- Project start date

- Project end date

At the beginning of each entry, the date, start time, weather, names of all sampling team members present, and the signature of the person making the entry will be documented. Measurements made and samples collected will be recorded. When a sample is collected or a measurement is made, a detailed description of the location of the station shall be recorded. The number of all photographs taken will also be noted. Equipment used to make measurements will be identified, along with the date of calibration.

All entries will be made in ink and no erasures will be allowed. If an incorrect entry is made, the information will be crossed out with a single strike mark and initialed. Blank pages will be noted as being intentionally blank.

Samples will be collected following the sampling procedures documented in the field sampling SOPs located in Appendix C. Equipment used to collect samples will be noted, along with the time of sampling, sample description, parameters being analyzed, and number of containers. Unique sample identification numbers (IDs) will be assigned to each sample. Field duplicate samples, which will receive an entirely separate sample ID, will be noted in the field logbook.

Field personnel will provide comprehensive documentation covering all aspects of field sampling, field analysis, and sample chain-of-custody (COC). This documentation constitutes a record that allows reconstruction of all field events to aid in the data review and interpretation process. All documents, records, and information relating to the performance of the field work will be retained in the project file.

1.7.2 Data Reporting

For the purposes of this investigation, two levels of data reporting have been defined:

- **Level 1**—Field Data, Treatment System Test Data and Health and Safety Reporting. This level of minimal or "results only" reporting is used for the field data, treatment system performance data (non-permit required data) and health and safety monitoring. This is because they do not generate or require extensive supporting documentation.
- **Level 2**—Analytical Reporting. Full "CLP-equivalent" reporting is required for all non-field data.

1.7.2.1 Field Data Reporting

Information collected in the field through visual observation, manual measurement, and/or field instrumentation will be recorded in field notebooks and then entered into an electronic data log. Data will be reviewed by the FTL or project chemist for adherence to this QAPP and consistency of data. Any concerns identified as a result of this review will be discussed with the QA Manager, corrected if possible, and incorporated into the data evaluation process.

Field data calculations, transfers, and interpretations will be conducted by the field crew and reviewed for accuracy by the FTL or project chemist. The appropriate task manager will review field documentation, data reduction, and accuracy of data entries into the data log. The data logs and documents will be checked for:

- General completeness

- Readability
- Use of appropriate procedures
- Whether modifications to sampling procedures are clearly stated
- Appropriate instrument calibration and maintenance records
- Reasonability of data collected
- Correctness of sample locations
- Correctness of reporting units, calculations, and interpretations

Where appropriate, field data forms and calculations will be processed and included in appendixes to the report. Original field logs, documents, and data reductions will be kept in the project file.

1.7.2.2 Laboratory Data Reporting

Calculations for analyses are based on regression analysis of calibration curves. Regression analysis is used to fit a curve through calibration standard data. Sample concentrations are calculated using the resulting regression equations.

Whenever possible, analytical data will be transferred directly from the instrument to a computerized data system. Raw data will be stored electronically and a hard copy file will be maintained. Laboratory data entry will be sufficient to document information used to arrive at reported values.

Electronic data storage shall be used when possible. All electronic data shall be maintained in a manner that prevents inadvertent loss, corruption, and inappropriate alteration. Electronic data shall be accessible and retrievable for a period of 10 years after project completion.

Raw data will be examined to assess compliance with QC guidelines stated in the appropriate SAS request forms located in Appendix A and the analytical SOPs stated in Appendix B. Surrogate, matrix spike, and QC check sample recoveries will be checked. In addition, samples and lab blanks will be checked for possible contamination or interferences. Chromatograms (where applicable) and concentrations will be checked to ensure that sample results are within the calibration range; if necessary, dilutions will be performed as defined by the initial calibration range.

Any deviations from stated guidelines would call for corrective action. Deviations caused by factors outside the laboratory's control, such as matrix interference, will be noted with an explanation in the report narrative. Calculations will be checked and the report reviewed for errors and oversights.

Upon completion, a report will be reviewed for discrepancies, errors, or omissions. Data will then be submitted to the Laboratory QA Manager for review and approval. The Laboratory QA Manager will review the package, see that any necessary corrections are made, and will give the package to the Laboratory Project Manager for review. A copy of the data package will be filed in the project file. Mailed data packages, along with applicable electronic data deliverables (EDDs), will be sealed in an appropriate shipping container with a custody seal and logged into a document mailing log.

All laboratory hard copy data deliverables will be submitted by the offsite laboratory in the format specified in the Special Analytical Services (SAS) request forms located in Appendix A of this QAPP.

1.7.3 Electronic Analytical Record Format

CH2M HILL will request that one ASCII text file be generated by the offsite laboratory for each sample delivery group (SDG). The file would be named "*.txt," where "*" represents the batch SDG number. Specific instructions regarding the ASCII text file will be communicated to the laboratory in the laboratory contract or SOW.

1.7.4 Project Record Maintenance and Storage

Project records will be stored and maintained in accordance with CH2M HILL's Data Management Plan (DMP) discussed in Section 2.10 of this QAPP. Each project team member is responsible for filing all project information or providing it to the project assistant familiar with the project filing system. Individual team members may maintain separate files or notebooks for individual tasks but must provide such files to the project file room upon completion of each task.

The general project file categories are as follows:

- Correspondence
- Non-laboratory project invoices and approvals by Vendor
- Original Unbound Reports
- Non-laboratory Requests for Proposals (RFPs), Bids, Contracts, and SOWs
- Field Data
- Data Evaluation and Calculations
- Site Reports from Others
- Bound Report Copies of Category C
- Photographs
- Insurance Documentation
- Laboratory Analytical Data and associated Documents/Memos
- Regulatory Submittals, Licensing, and Permitting Applications
- Site and Reference Material
- Health and Safety Plans
- Figures and Drawings

A project-specific index of file contents is kept with the project files at all times.

SECTION 2

Data Generation and Acquisition

This section describes the procedures for acquiring, collecting, handling, measuring, and managing data in support of this sampling activity. It addresses the following aspects of data generation and acquisition:

- Sampling process design
- Sampling method requirements
- Sample handling and custody requirements
- Laboratory analytical methods requirements
- Laboratory QC requirements
- Field and laboratory instrument calibration and frequency
- Inspection and acceptance requirements for supplies and consumables
- Data acquisition requirements
- Data management
- Field and laboratory instrument and equipment testing, inspection, and maintenance requirements

2.1 Sampling Process Design

The sampling locations and frequency of collection were chosen to best fulfill the project objectives stated in Step 2 of the DQO process. The sampling design consists of three parts: monitoring and residential well sampling, WPDES Permit sampling, and bioventing process assessment sampling.

2.1.1 Monitoring and Residential Well Sampling

The monitoring and residential well sampling design was selected to assess the effectiveness of LNAPL removal and groundwater treatment and to assess the degree of natural attenuation. The monitoring wells to be sampled include: MW-1, MW-2, MW-3, MW-4, MW-5, MW-6S, MW-7, MW-8, MW-9, MW-10, MW-10S, MW-11, MW-12, MW-13, MW-14, MW-15, MW-16, MW-17, MW-19, MW-20, MW-21, MW-22, MW-23, MW-24, MW-25, and MW-26. The sampling schedule is located in Table 2-1.

TABLE 2-1
LTRA Tentative Sampling Schedule
Penta Wood Products – Siren Wisconsin

Sampling Event Type	Samples	QC Samples				Total Number of Samples*
		Dup	MS	MSD	FB	
April 2001 Semi-Annual Sampling	19 mon. wells and 4 res. Wells	3	2	2	2	32
June 2001 Quarterly Sampling	5 mon. wells	1	1	1	1	9
September 2001 Annual Sampling	19 mon. wells, 4 res. wells and soil gas	3	2	2	2	32
December 2001 Quarterly Sampling	5 mon. wells	1	1	1	1	9
March 2002 Semi-Annual Sampling	5 mon. wells and 4 res. Wells	1	1	1	1	13
June 2002 Quarterly Sampling	5 mon. wells	1	1	1	1	9
September 2002 Annual Sampling	19 mon. wells, 4 res. wells and soil gas	3	2	2	2	32
December 2002 Quarterly Sampling	5 mon. wells	1	1	1	1	9
March 2003 Semi-Annual Sampling	5 mon. wells and 4 res. Wells	1	1	1	1	13
June 2003 Quarterly Sampling	5 mon. wells	1	1	1	1	9
September 2003 Annual Sampling	19 mon. wells, 4 res. wells, soil gas, 18 soil samples	5	3	3	3	55

* Total number is estimated and is subject to change. Soil gas samples are a field measurement and not counted in sample count.

The monitoring wells will be sampled in April 2001 and then annually thereafter, starting in September 2001, for PCP, BTEX, naphthalene, TAL metals, and the following natural attenuation parameters:

- Dissolved Oxygen (DO)
- pH, temperature, and specific conductance
- Oxidation/reduction potential (ORP)
- Alkalinity
- Total organic carbon (TOC)
- Hardness
- Methane
- Nitrate and Nitrite nitrogen
- Sulfate and Sulfite sulfur
- Total iron and ferrous iron
- Manganese

- Carbon dioxide (CO_2)
- Chloride

A smaller set of five monitoring wells will be sampled and analyzed for the parameters listed above on a quarterly basis. The specific wells sampled will be chosen jointly by CH2M HILL, USEPA, and the WDNR based on observations from previous sampling events and trend analysis. However, MW26 will be monitored during each quarterly sampling event to monitor groundwater concentrations underneath the infiltration basin. Water-level elevations will be taken in all wells on a quarterly basis. LNAPL thickness will be measured in extraction well nest EW-03, EW-04, EW-06, and EW-10 on a quarterly basis. Monitoring wells MW10, MW10S, MW18, MW19, and MW20 will also be monitored for LNAPL thickness on a quarterly basis until LNAPL is no longer detected.

The four residential wells that will be sampled annually are those listed in Table 2-2.

TABLE 2-2
LTRA Residential Well Information
Penta Wood Products – Siren, Wisconsin

Location ID	Resident Name	Resident Address	Resident Phone Number	WI Well #
RW01	Unknown (formerly Skold)	8713 Daniels 70	Unknown	FG508
RW02	Bud & LaVonne Brethorst	8627 Daniels 70	(715) 349-5237	FG506
RW03	Nelson	Cabin on Engstrom property	Unknown	JB 251
RW04	Vayne Engstrom	8526 Daniels 70	(715) 349-5212	AN547

2.1.2 Groundwater Treatment System Monitoring

The groundwater treatment system influent will be monitored for PCP on a monthly basis. The effluent is discharged to the infiltration basing in accordance with the effluent limitations, monitoring requirements, and other conditions specified in the WPDES permit. The required parameters and their frequency of collection as well as the required methodologies are summarized in Table 2-3.

TABLE 2-3
WPDES Permit Sampling Requirements
Penta Wood Products – Siren, Wisconsin

Parameter	Method	Frequency of Collection
Influent		
Pentachlorophenol (PCP)	SW-846 8151/8270[1]	Monthly
Effluent		
PCP	SW-846 8151/8270[1]	Weekly
pH field	Field Measurement	Monthly for first quarter

TABLE 2-3
WPDES Permit Sampling Requirements
Penta Wood Products – Siren, Wisconsin

Parameter	Method	Frequency of Collection
		Quarterly
Total Suspended Solids (TSS)	EPA 160.2	Monthly for first quarter
		Quarterly
Chloride	EPA 325.1	Quarterly
Diesel Range Organics (DRO)	Wis. Mod. DRO	Monthly
Total Organic Carbon	SW-846 9060	Monthly
1,3,5-Trimethylbenzene	SW-846 8260	Monthly for first quarter
		Quarterly
1,2,4-Trimethylbenzene	SW-846 8260	Monthly for first quarter
		Quarterly
Total Trimethylbenzenes	SW-846 8260	Monthly for first quarter
		Quarterly
2,3,7,7-TCDD	SW-846 8290	Monthly for first year
		Quarterly
Phenol (total)	SW-846 8270	Monthly
Naphthalene	SW-846 8270	Monthly
Benzene	SW-846 8260	Monthly for first year
		Quarterly
Ethylbenzene	SW-846 8260	Monthly for first quarter
		Quarterly
Toluene	SW-846 8260	Monthly for first quarter
		Quarterly
Xylene	SW-846 8260	Monthly for first quarter
		Quarterly
Total Arsenic	SW-846 6010	Monthly for first year
		Quarterly
Total Copper	SW-846 6010	Monthly for first quarter
		Quarterly
Total Zinc	SW-846 6010	Monthly for first quarter
		Quarterly

TABLE 2-3
WPDES Permit Sampling Requirements
Penta Wood Products – Siren, Wisconsin

Parameter	Method	Frequency of Collection
Total Iron	SW-846 6010	Quarterly
Total Manganese	SW-846 6010	Quarterly
Acid Extractables	EPA 625	Annually
Dioxins and Furans	SW-846 8290	Annually

1 = SW-846 method 8270 may be employed for those samples requiring a faster turn around time. SW-846 method 8151 will be used to detect PCP to a limit of 0.1 µg/L.
Acid Extractables = 4-chloro-3-methylphenol
2-chlorophenol
2,4-dchlorophenol
2,4-dimethylphenol
2,4-dinitrophenol
2-methyl-4,6-dinitrophenol
2-nitrophenol
4-nitrophenol
pentachlorophenol
phenol
2,4,6-trichlorophenol
Dioxins and Furans = Total TCDD
Total TCDF
Total PeCDD
Total PeCDF
Total HxCCD
Total HeCCF

Sampling procedures shall be performed in accordance with Chapter 218 of the Wis. Adm. Code.

2.1.3 Biovent System Monitoring

Soil and soil gas samples will be collected and analyzed to assess the degree and effectiveness of PCP removal. Soil gas analysis will conducted annually once the system is up and running. Analyses for oxygen, carbon dioxide, temperature, and humidity will be measured in the soil gas wells. Soil samples will be collected at various depths within the PCP-portion of the CAMU and analyzed for PCP, TPH, and DRO. Table 2-4 summarized the anticipated number of samples.

TABLE 2-4
Biovent System Monitoring Sampling
Penta Wood Products – Siren, Wisconsin

Sample Matrix	Field Samples	Field QC				Total Number of Samples
		FB	Dup	MS	MSD	
Bioventing Soil Gas Analysis	63	—	—	—	—	63
Soil	18	—	2	—	—	20

2.1.4 Waste Disposal Characterization

Waste disposal characterization samples were collected from the product storage tank at the site and spent clay and carbon were analyzed for PCP, TCDDs, and TCDFs, and parameters deemed necessary by the receiving disposal facility. The composite samples were analyzed by a laboratory contracted to the waste disposal subcontractor, Safety Kleen.

2.1.5 Water Level Measurements

Water level measurements are measured continually via transducers in the groundwater extraction wells (EW-2 through EW-7, EW-10, and EW-11) to assess the draw down of the aquifer during treatment system operation. Water levels will be taken in the monitoring wells during monitoring well sampling events.

Product levels will be taken at the extraction wells using an oil/water interface probe to assess LNAPL thickness.

2.1.6 Field Parameters

DO, pH, oxidation/reductive potential, temperature, and specific conductance measurements will be taken at each well during sampling. Three well volumes will be extracted from each well prior to sampling and the filed parameter readings will be documented after each well volume is extracted.

2.2 Sampling Method Requirements

SOPs for field sampling method and decontamination procedures are contained in Appendix C; these include:

- pH
- Temperature and conductivity
- Redox potential
- PID monitoring
- Field filtering
- DO
- Water level measurement and well purging
- Soil vapor parameters

- Monitoring Well Sampling
- Soil Gas pressure
- Decontamination

Prior to sampling at a station, re-usable (i.e., non-dedicated) sampling equipment will be scrubbed with Alconox, rinsed with distilled water, rinsed with methanol, rinsed with distilled water again, and air-dried. Large sampling equipment will be washed with a high-pressure water wash using a brush as necessary, to remove any particles. Field blanks will be collected by passing HPLC grade laboratory water over decontaminated sampling equipment. The field blanks will then be analyzed for the same parameters as the field samples to assess the effectiveness of the decontamination procedures. Details are provided in Appendix C.

2.3 Sample Handling and Custody Requirements

2.3.1 Sample Handling and Preservation

Sample handling, preservation, and storage procedures that will be used for the laboratory investigations are presented in Tables 2-5 and 2-6. Sample containers will be provided by the subcontracted laboratory and prepared in accordance with USEPA guidelines (USEPA, 1994a) prior to field operations. Sample containers will be purchased by the laboratory pre-cleaned to requirements of the USEPA Office of Solid Waste and Emergency Response (OSWER) Directive 9240.05A. Sample containers will be kept closed and in a cooler until used. As sample containers are filled, they will be labeled with USEPA sample tags, pertinent information recorded in the field notebook and COC forms, and bottles transported on ice in coolers.

Corrective actions will be taken as soon as a problem is identified and may include discontinuing the use of a specific bottle lot, contacting the bottle supplier(s) for retesting the representative bottle from a suspect lot, resampling the suspected samples, and validating the data, taking into account that the contaminants could be introduced by the laboratory (i.e., common lab solvents, sample handling artifacts, etc.) as a bottle QC problem, and educated determination of whether the bottles and data are still usable must be made

TABLE 2-5
LTRA Sample Containers, Preservatives, and Holding Times
Penta Wood Products – Siren, Wisconsin

Sample Matrix	Parameter	Bottle Type	Preservation	Holding Time
Groundwater – Monitoring Wells and Extraction Wells	PCP	1 1-L amber glass	4°C	7 days to extraction and 40 days from extraction to analysis
	BTEX	3 x 40-mL VOA vials	HCL to pH<2, 4ºC	14 days
	Naphthalene	1 1-L amber glass	4ºC	7 days to extraction and 40 days from extraction to analysis

TABLE 2-5
LTRA Sample Containers, Preservatives, and Holding Times
Penta Wood Products – Siren, Wisconsin

Sample Matrix	Parameter	Bottle Type	Preservation	Holding Time
	Total Metals	500-mL poly	HNO_3 to pH <2, 4ºC	180 days
	Dissolved Metals	500-mL poly	HNO_3 to pH <2, 4ºC	180 days
	Alkalinity	250-mL poly	4ºC	14 days
	Nitrate[1]	1 1-L poly	4ºC	48 hours
	Sulfate[1]	1 1-L poly	4ºC	28 hours
	Sulfide	1 1-L amber glass	NaOH to pH>9, Zn acetate, 4ºC	7 days
	Chloride[1]	1 1-L poly	4ºC	28 days
	Hardness	100-mL poly	HNO_3 to pH <2, 4ºC	6 months
	TOC	250-mL poly	HCL to pH < 2, 4ºC	28 days
	Methane	3 x 4-mL VOA vials	4ºC	14 days
Waste –LNAPL	DRO	4 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	HxCDDs[2]	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	HxCDFs[2]	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	PeCDDs[2]	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	PeCDFs[2]	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	TCDDs[2]	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	TCDFs[2]	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	PCP	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis

TABLE 2-5
LTRA Sample Containers, Preservatives, and Holding Times
Penta Wood Products – Siren, Wisconsin

Sample Matrix	Parameter	Bottle Type	Preservation	Holding Time
	Phenol	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	2,3,4,6-Tetrachlorophenol[3]	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	2,4,6-Trichlorophenol[3]	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	2,4-Dimethylphenol[3]	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
Soil	PCP	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	TPH	8 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis
	DRO	4 oz. glass jar	4ºC	14 days to extraction and 40 days from extraction to analysis

1,2,3 = Parameters may be collected in the same sample container

TABLE 2-6
WPDES Permit Required Preservation and Holding Times
Penta Wood Products – Siren, Wisconsin

Parameter	Bottle Type	Preservation	Holding Time
PCP	1 1-L amber glass	4°C	7 days to extraction and 40 days from extraction to analysis
pH	Field measurement	NR	Immediately
TSS	500-mL poly	4°C	7 days
Chloride	250-mL poly	4ºC	28 days
DRO	1-L amber glass	HCL to pH <2, 4ºC	7 days to extraction and 40 days from extraction to analysis
TOC	250-mL poly	HCL to pH < 2, 4ºC	28 days
Trimethyl Benzenes[1]	3 x 40-mL VOA vials	HCL to pH<2, 4ºC	14 days

TABLE 2-6
WPDES Permit Required Preservation and Holding Times
Penta Wood Products – Siren, Wisconsin

Parameter	Bottle Type	Preservation	Holding Time
2,3,7,8-TCDD	3 x 40-mL VOA vials	HCL to pH<2, 4ºC	14 days
Phenol (total)	1 1-L amber glass	4°C	7 days to extraction and 40 days from extraction to analysis
Naphthalene	1 1-L amber glass	4°C	7 days to extraction and 40 days from extraction to analysis
BTEX[2]	3 x 40-mL VOA vials	HCL to pH<2, 4ºC	14 days
Total Metals[3]	500-mL poly	HNO_3 to pH <2, 4ºC	180 days
Acid Extractables[4]	1 1-L amber glass	4°C	7 days to extraction and 40 days from extraction to analysis
Dioxins and Furans[5]	1 1-L amber glass	4°C	7 days to extraction and 40 days from extraction to analysis

1 = 1,3,5-trimethylbenzene; 1,2,4-trimethylbenzene; total trimethylbenzenes
2 = benzene, toluene, ethylbenzene, xylenes (total)
3 = arsenic, copper, zinc, iron
4 = 4-chloro-3-methylphenol; 2-chlorophenol; 2,4-dichlorophenol; 2,4-dimethylphenol; 2-methyl-4,6-dinitrophenol; 2-nitrophenol; 4-nitrophenol; pentachlorophenol; phenol; 2,4,6-trichlorophenol
5= total TCDD; total TCDF; total PeCDD; total PeCDF; total HxCCd; total HxCCF

2.3.2 Sample Identification System

A sample-numbering system devised by CH2M HILL will be used to identify each sample, including duplicates and blanks. A Sample Management Office (SMO) number and a Central Regional Laboratory (CRL) number will be assigned to each sample to be analyzed by an offsite laboratory. (Refer to the *User's Guide to the Contract Laboratory Program* for an explanation of the SMO numbers. Refer to the CRL *Sample Handling Manual* for an explanation of the CRL number.) The Field Activity Manager will maintain a listing of sample IDs in the sampling logbook. Each CH2M HILL sample number will consist of three components.

Each sample will have a three-digit, project identification code (identifying PWP as Penta Wood Products), followed by an alphanumeric code corresponding to the media, and a three-digit, sequential number. Sample numbers will be reserved for the different media being sampled. They will not be repeated within a sample station, media, or among differing media. Duplicate samples will not be distinguished within the sample numbers, but will be distinguished through the subsample identification within the sample tracking and data management systems. This is done so that no bias is given to the samples during analysis. The media codes and reserved sample numbers are as follows:

- SS – Surface (0 to 2 feet) soil sample
- SB – Subsurface Soil (> 2 feet) soil sample
- MW – Monitoring well groundwater sample
- RW – Residential well groundwater sample
- EW – Extraction well groundwater sample

- LN – LNAPL sample
- SG – Soil gas sample
- IF – Influent to treatment system sample
- EF – Effluent to treatment system sample
- TR – Treatment residuals sample
- OBEF – Oil bag filter effluent treatment system sample
- OSW – Oil/water separator effluent treatment system sample
- PBEF – Particulate bag filter effluent treatment system sample
- C1EF – Carbon 1 effluent treatment system sample
- C2EF – Carbon 2 effluent treatment system sample
- CEF – Clay effluent treatment system sample
- FB – Field blank QC sample
- FD – Field duplicate QC sample

Examples of sample numbers are as follows:

- PWPMW0101 – Groundwater sample collected from PWP sample location MW01, sample number 01.
- PWPSB1011-5.0 – Subsurface soil sample collected from PWP sample location B10, sample number 11, collection starting at 5 feet bgs.

2.3.3 Sample Packaging

Sample packaging and shipping procedures are designed to ensure that the samples will arrive at the laboratory intact, along with their COC forms. Sample tags and COC forms will be produced by the software *Forms II Lite*. An example COC form and sample tag is located in Appendix D of this QAPP. Samples will be packaged for shipment as outlined below:

- All sample containers will have affixed sample tags.
- Caps on the sample containers will be checked to ensure they are properly sealed.
- Sample container caps will be wrapped with clear packing tape to prevent them from becoming loose.
- COC forms will be completed with required sampling information, and recorded information will match the sample tags.
- If the designated sampler relinquishes samples to another sampling or field crew member for packing or other purposes, the sampler will complete the COC forms prior to this transfer.
- Appropriate personnel will sign and date COC forms to document the sample custody transfer.
- The outside drain plug at the bottom of the cooler will be secured inside and out using duct tape.
- Sample containers will be protected in bubble wrap or other cushioning material. One to 2 inches of cushioning material will be placed at the bottom of the cooler.

- Sealed sample containers will be placed in the cooler.
- Ice will be double bagged with plastic zipper bags. Bags will be sealed and placed loosely in the cooler. Remaining space in the cooler will be filled with cushioning material.
- COC forms will be placed in a sealed plastic bag and taped to the inside of the cooler lid.
- Temperature blanks will accompany all samples transported to the laboratory.
- The lid of the cooler will be closed, locked, and secured with strapping tape. Strapping tape will be wrapped around both ends of the cooler at least twice.
- The cooler will be marked on the outside with the following information: shipping address, return address, "Fragile" labels, and arrows indicating "this side up."
- Labels will be covered with clear plastic tape.
- Signed custody seals will be signed, dated, and placed over opposite corners of the cooler lid and covered with clear plastic tape.
- All coolers will be shipped by express overnight service or sent by courier to the analytical laboratory(s).
- All samples will be transported or shipped in a manner that protects integrity of the samples and safety of the handlers.
- Original COC forms will accompany the shipment; copies will be retained by the sampler for sampling records.
- If samples are sent by common carrier, bills of lading will be used. Receipts or bills of lading will be retained as part of the permanent project documentation.
- Commercial carriers will not be required to sign off on COC forms as long as the forms are sealed inside the sample cooler and custody seals remain intact.
- Packaging, marking, labeling, and shipping of samples will comply with the regulations promulgated by the U.S. Department of Transportation in the Code of Federal Regulations (49 CFR 171-177).
- Field samples will be analyzed as soon as possible after receipt at the laboratory. Maximum sample holding times are stipulated in Tables 2-5 and 2-6.

Disposable equipment and debris such as health and safety equipment, plastic sheeting, sampling equipment, and other equipment and/or sampling debris that has come into contact with sample media, will be collected in plastic bags during the sampling events and placed into appropriately labeled containers.

Decontamination rinsate (e.g., tap and distilled water containing small amounts of solvent) will be containerized at each sampling location or group of locations. Upon completion of the field activities, the rinsate and other generated waste will be discarded appropriately in accordance with applicable rules and regulations.

2.3.3.1 Shipping Airbills

If samples are shipped, airbills will be retained to provide a record for sample shipment to the laboratory. Completed airbills will accompany shipped samples to the laboratory and will be forwarded along with data packages. The airbill number will be documented on the COC form accompanying the samples to the laboratory for sample tracking purposes. Airbills will be kept as part of the data packages in the project files.

2.3.4 Sample Custody

Accurate records and control of sample and data custody are necessary to provide relevant and defensible data. COC is addressed during field sample collection, data analyses in the laboratory, and through proper handling of project files. Persons will be considered to have custody of samples when samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured to prevent tampering. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel.

COC forms will provide the record of responsibility for sample collection, transport, and submittal to the laboratory. Field personnel designated as responsible for sample custody will fill out COC forms at each sampling site, at a group of sampling sites, or at the end of each day of sampling. In the event that samples are relinquished by the designated sampling person to other sampling or field personnel, COC forms will be signed and dated by the appropriate personnel to document the custody transfer. Original COC forms will accompany samples to the laboratory, and copies will be forwarded to the project files.

2.3.4.1 Field Custody Procedures

COC forms will be required for all samples. The sampling crew in the field will initiate COC forms. COC forms will contain the sample's unique ID, sample date and time, sample description, sample type, preservation (if any), and analyses required. Original COC forms, signed by the sampling crew, will accompany the samples to the laboratory. A copy of relinquished COC forms will be retained with the field documentation. COC forms will remain with the samples at all times. Samples and signed COC forms will remain in the possession of the sampling crew until samples are delivered to the express carrier (e.g., Federal Express), hand delivered to the laboratory, or placed in secure storage.

2.3.4.2 Laboratory Custody Procedures

Laboratory custody procedures will be in place to ensure the integrity of sample and laboratory data handling. Laboratory custody procedures are defined in the laboratory's COC SOP located in Appendix B of this QAPP.

2.3.4.3 Laboratory Sample Receipt

Upon sample receipt, the Laboratory Sample Custodian will verify package seals, open the packages, check temperature blanks (and record temperatures), verify sample integrity, and inspect contents against COC forms. The Laboratory Project Manager will be contacted to resolve any discrepancies between sample containers and COC forms. Once the shipment and COC form are in agreement, the Sample Custodian will initiate an internal COC form as well as supply the laboratory task manager with a sample acknowledgement letter. When

applicable, sample preservation will be checked and pH documented. If the sample temperatures are outside the required range, the laboratory will contact the project manager or the contractor as to the proper course of action.

Samples will be logged into the Laboratory Information Management System (LIMS), which assigns a unique laboratory number to each sample. LIMS will be used by all laboratory personnel handling samples, to ensure all sample information is captured. Analyses required will be specified by codes assigned to samples at log-in. Labels containing the laboratory sample number are generated and placed on sample bottles.

2.3.4.4 Laboratory Sample Storage

After the laboratory labels the samples, they will be moved to locked refrigerators where they will be maintained at 4°C. Soil samples may be frozen. If soil samples are frozen, the holding time stops accumulating at the time the sample freezes, and begins accumulating again at the time the sample begins to thaw. Access to refrigerators will be limited to members of the sample management department.

When samples are required, an appropriate member of the sample management department will locate the samples in the locked refrigerator, sign and date the internal sample tracking form and provide the sample(s) to the analyst. When the analyst is finished with samples, unused portions will be returned to an appropriate member of the sample management department for replacement in a secure refrigerator. The analyst will sign and date internal COC forms. In the event that entire samples are depleted during analysis, a notation of "sample depleted" or "entire sample used" will be made on the internal COC forms.

Sample extracts will be stored in designated secure, refrigerated storage areas. Samples and sample extracts will be maintained in secure storage until disposal. No samples or extracts will be disposed of without prior written approval from an appropriate member of the Project Team. The Sample Custodian will note sample disposal date in the sample ledger. The laboratory will dispose of samples in accordance with applicable regulations.

2.3.4.5 Laboratory Logbooks

Workbooks, bench sheets, instrument logbooks, and instrument printouts will be used to trace the history of samples through the analytical process and document important aspects of the work, including associated QCs. As such, all logbooks, bench sheets, instrument logs, and instrument printouts will be part of the permanent record of the laboratory. In addition, relevant information will be entered into the LIMS at the time information is generated.

Each page or entry will be dated and initialed by the analyst at the time of entry. Errors in entry will be crossed out in indelible ink with a single stroke, corrected without obliterating or writing directly over the erroneous entry, and initialed and dated by the individual making the correction. Lining out unused portions and initialing by the person lining out the page will complete pages of logbooks that are not used.

The analyst will record information regarding the sample, the analytical procedures performed, and the results on laboratory forms or personal notebook pages, and enter this information in LIMS. These notes will be dated and will identify the analyst, instruments used, and instrument conditions.

Sufficient raw data records must be retained to permit reconstruction of initial instrument calibrations (e.g., calibration date, test method, instrument, analysis date, each analyte name, concentrations and responses, calibration curves, response factors, or unique equations or coefficients used to reduce instrument responses into concentrations).

Laboratory notebooks will be reviewed periodically by the laboratory group leaders for accuracy, completeness, and compliance with this QAPP. The laboratory group leader will verify all entries and calculations. If all entries on the pages are correct, the laboratory group leader will initial and date the pages. Corrective action will be taken for incorrect entries before the laboratory group leader signs.

2.3.4.6 Laboratory Project File

Documentation will be placed in a single, secured project file, which will be maintained by the Laboratory Project Manager. This file will consist of the following components, all filed chronologically:

- Agreements
- Correspondence
- Memos
- Notes and Data

Reports (including QA reports) will be filed with correspondence. Analytical laboratory documentation and field data will be filed with notes and data. Filed materials may only be removed by authorized personnel on a temporary basis. The name of the person removing the file will be recorded. Laboratories will retain will project files and data packages for a minimum of 7 years unless otherwise agreed upon.

2.3.4.6 Computer Tape and Hard Copy Storage

All electronic files will be maintained on CD-ROM (preferred media), magnetic tape or diskette for ten years; hard copy data packages (including chromatograms) will be maintained in files for 7 years. The computer tape and hard copy storage should include notation of instrument run files and calibration.

2.4 Analytical Method Requirements

Once the samples have been properly collected and documented, they will be sent to the offsite laboratory for analysis. Since April 2000 PEL Laboratories, Inc. of Tampa, Florida has been performing the analyses for the PWP site. PEL Laboratories, Inc. will continue to perform all of the required analyses at the PWP site until September 29, 2001, at which time their subcontract ends. A NR 149 Wis. Adm. Code certified laboratory will be selected to perform the analyses at the PWP site after September 29, 2001. The analytical laboratories will be chosen both on required certification and on their ability to perform the analyses with a high level of analytical quality.

The analytical methods chosen are those that meet the requirements of the WPDES permit and meet the required level of quantification (LOQ). Table 2-7 list the required methodologies and limits of quantification for the analyses to be performed during the LTRA, excluding the wastewater treatment plant monitoring. The WPDES permit requires

that the analytical methods be chosen as to follow the criteria stated in NR 219 Wis. Adm. Code. The NR 219 Wis. Adm. Code references SW-846 method 8270 as an acceptable method for the analysis of PCP. Due to the low PAL of 0.1 µg/L for PCP, SW-846 8270 is an insufficient method. SW-846 method 8151 will be used to report PCP down to the WPDES required LOQ of 0.1 µg/L. The required analytical methods for the WPDES sampling are found in Table 2-3. The wastewater treatment plant required Limits of Detection are based on NR 140 Wis. Adm. Code PALs. Most of the parameters listed in the WPDES permit do not have stated effluent limitations. These parameters were given a LOQ at or below the PAL. However, some of the WPDES required parameters do not have documented PALs. These parameters were given a method recommended LOQ. The LOQs for the WPDES permit sampling are listed in Table 2-8.

TABLE 2-7
LTRA Parameter List and Contract Required Limits of Quantification (LOQs)
Penta Wood Products – Siren, Wisconsin

Sample Matrix	Parameter	Analytical Method	LOQ (µg/L)
Groundwater – Monitoring Wells and Extraction Wells	PCP	SW-846 8015	0.1
	BTEX	SW-846 8260	0.5 for Benzene, 1.0 for others
	Naphthalene	SW-846 8270	5.0
	Total Metals	SW-846 6010/7000 series	Arsenic = 1.0 Copper = 25 Iron = 25 Manganese = 15 Zinc = 25
	Dissolved Metals	SW-846 6010/7000 series	Arsenic = 1.0 Copper = 25 Iron = 25 Manganese = 15 Zinc = 25
	Alkalinity	EPA 310.1	5.0 mg/L
	Nitrate	EPA 353.2	1 mg/L
	Sulfate	EPA 375.1	10 mg/L
	Sulfide	EPA 376.1	1.0 mg/L
	Chloride	EPA 325.1	1.0 mg/L
	Hardness	EPA 130.1	500 µg/L
	TOC	SW-845 9060	1.0 mg/L
	Methane	RSK 175	10 µg/L
Waste –LNAPL	DRO	Wis. Mod. DRO	1.0 mg/L
	HxCDDs	SW-846 8290	0.0063
	HxCDFs	SW-846 8290	0.0063
	PeCDDs	SW-846 8290	0.0063

TABLE 2-7
LTRA Parameter List and Contract Required Limits of Quantification (LOQs)
Penta Wood Products – Siren, Wisconsin

Sample Matrix	Parameter	Analytical Method	LOQ (µg/L)
	PeCDFs	SW-846 8290	0.0035
	TCDDs	SW-846 8290	0.0063
	TCDFs	SW-846 8290	0.0063
	PCP	SW-846 8151	0.1
	Phenol	SW-846 8270	5.0
	2,3,4,6-Tetrachlorophenol	EPA 625	4.0
	2,4,6-Trichlorophenol	EPA 625	3.0
	2,4-Dimethylphenol	EPA 625	3.0
Soil	PCP	SW-846 8270	0.5 mg/kg
	TPH	EPA 418.1	10 mg/kg
	DRO	Wis. Mod. DRO	1 mg/kg

TABLE 2-8
WPDES Permit Sampling LOQs
Penta Wood Products – Siren, Wisconsin

Parameter	WPDES LOQ	PAL	SAS Required LOQ
Pentachlorophenol (Influent)	µg/L[a]	0.1 µg/L	0.1 µg/L
Pentachlorophenol (Effluent)	0.1 µg/L (monthly average)	0.1 µg/L	0.1 µg/L
PH	Su	+- 1 unit	NA
TSS	mg/L[a]	NL	4.0 mg/L
Chloride	mg/L[a]	125 mg/L	1.0 mg/L
DRO	mg/L[a]	NL	1.0 mg/L
TOC	mg/L[a]	+- 1 mg/L	1.0 mg/L
1,3,5-Trimethylbenzene	µg/L[a]	96 µg/L[b]	5.0 µg/L
1,2,4-Trimethylbenzene	µg/L[a]	96 µg/L[b]	5.0 µg/L
Total Trimethylbenzene	µg/L[a]	96 µg/L	10.0 µg/L

TABLE 2-8
WPDES Permit Sampling LOQs
Penta Wood Products – Siren, Wisconsin

Parameter	WPDES LOQ	PAL	SAS Required LOQ
2,3,7,8 – TCDD	0.000003 µg/L (monthly average)	0.000003 µg/L	0.000003 µg/L
Phenol	µg/L[a]	1.2 mg/L	5.0 µg/L (total phenol)
Naphthalene	8.0 µg/L (monthly average)	8 µg/L	5.0 µg/L
Benzene	0.5 µg/L (monthly average)	0.5 µg/L	0.5 µg/L
Ethylbenzene	µg/L[a]	0.7 mg/L	5.0 µg/L
Toluene	µg/L[a]	0.2 mg/L	5.0 µg/L
Xylene	µg/L[a]	1 mg/L	5.0 µg/L
Total Arsenic	5.0 µg/L (monthly average)	5 µg/L	1.0 µg/L
Total Copper	µg/L[a]	130 µg/L	25 µg/L
Total Zinc	µg/L[a]	2.5 mg/L	25 µg/L
Total Iron	µg/L[a]	0.15 mg/L	25 µg/L
Total Manganese	µg/L[a]	0.025 mg/L	15 µg/L
Acid Extractables			
4-chloro-3-methylphenol	NL	NL	3.0 µg/L
2-chlorophenol	NL	NL	4.0 µg/L
2,4-dichlorophenol	NL	NL	3.0 µg/L
2,4-dimethylphenol	NL	NL	3.0 µg/L
2,4-dinitrophenol	NL	NL	43.0 µg/L
2-methyl-4,6-dinitrophenol	NL	NL	25.0 µg/L
2-nitrophenol	NL	NL	4.0 µg/L
4-nitrophenol	NL	NL	3.0 µg/L
Pentachlorophenol	NL	NL	4.0 µg//L
Phenol	NL	NL	3.0 µg/L
2,4,6-trichlorophenol	NL	NL	3.0 µg/L
Dioxins and Furans			0.0063 µg/L
Total TCDD	NL	NL	0.0063 µg/L
Total TCDF	NL	NL	0.0063 µg/L

TABLE 2-8
WPDES Permit Sampling LOQs
Penta Wood Products – Siren, Wisconsin

Parameter	WPDES LOQ	PAL	SAS Required LOQ
Total PeCDD	NL	NL	0.0063 µg/L
Total PeCDF	NL	NL	0.0035 µg/L
Total HxCCD	NL	NL	0.0063 µg/L
Total HxCCF	NL	NL	0.0063 µg/L

LOQ = Limit of Quantificalion
PAL = Preventive Action Limit (NR 140 Wis. Adm. Code)
NL = Not Listed
[a] = Only units of concentration were listed in the WPDES Permit No. WI-0061531-01-0
[b] = PAL is for total trimethylbenzenes

2.3.5 Analytical SOPs

Analytical SOPs are used by the laboratory to assure that the samples submitted are analyzed accurately and precisely. The analytical SOPs reflect the requirements of the stated methods while including internal QC criteria. If not otherwise stated within this QAPP, the QC criteria used during the analyses are those stated within the analytical SOPs. The PEL's analytical SOPs included in Appendix B are:

- Sample Management: Initial Receipt, Inventory, Preservation Verification, Labeling, and Storage
- Sample Management: Internal COC
- QC Activities: Corrective Action System
- Sample Preparation: Digestion of Liquid and Solid Samples for Cations Analyses
- Sample Preparation: SW-846 Herbicide Extraction for Method 8151/EPA 615
- Sample Preparation: SW-846 3510C Separatory Funnel Extraction
- Sample Preparation: SW-846 3550B Sonication
- Sample Analyisis: 625/8270C GC/MS Semi-Volatile Organics
- Sample Analysis: Alkalinity, Titrimetric (Method 310.1)
- Sample Analysis: TOC Method 415.1/9060 (total organic carbon, liquid and solid)
- Sample Analysis: Metals by GFAA (Graphite Furnace Atomic Absorption)
- Sample Analysis: GC/MS Volatile Organics (SW-846 8260B/EPA 624)
- Sample Analysis: Cations by ICP (EPA 200.7, 6010B, AFCEE 3.0, and CLP ILM04.0)

- Sample Analysis: Chlorophenoxy Acid Herbicides by Capillary Gas Chromatography (SW-846 8151)
- Sample Analysis: Chloride Method 325.2 (Colormetric, Automated Ferricyanide)
- Sample Analysis: Nitrogen, Nitrate Method 353.2 (Colormetric, Automated, Cadmium Reduction)
- Sample Analysis: Sulfate, Method EPA 375.4 (Turbidimetric)
- Sample Analysis: Titration Procedure for Sulfides.
- Sample Analysis: TSS Method EPA 160.2
- Sample Analysis: Aqueous and Soil Samples for Diesel Range Organics by Gas Chromatography by Method 8015 Modified.
- Analysis of Dissolved Gases in Water (Microseeps Laboratory – subcontract to PEL)
- Extraction of PCDD/PCDF from Water for Methods 1613, 8290, and 551 (Triangle Laboratories – subcontract to PEL)
- PCDDs and PCDFs by HRGC/HRMS – Method 8290 (Triangle Laboratory – subcontract to PEL)

2.4 Quality Control Requirements

The contracted analytical laboratory has a QC program to assess the reliability and validity of the analyses being performed. The purpose and creation of QC samples is discussed and summarized below. Tables 2-1 and 2-4 outline the anticipated field QC samples to be taken.

2.4.1 Quality Control Samples

Field QC samples will be collected to determine the accuracy and precision of the analytical results. The QC sample frequencies are stated below and summarized in Tables 2-1 and 2-2. Field QC samples are not required under the WPDES permit, therefore QC samples will not be collected for the treatment system sampling. All sampling activities will be conducted in accordance with the Health and Safety Plan and all sample-handling procedures will be in accordance with this QAPP. Tables 2-5 and 2-6 summarize sample containers, holding times, and preservation requirements.

Field blanks (FBs) will be collected to monitor cleanliness of sampling equipment and the effectiveness of decontamination procedures. Contamination from the sampling equipment can bias the analytical results high. FBs will be prepared by filling sample containers with laboratory-grade analyte-free water that has been passed through a decontaminated or unused disposable sampling device (see Appendix C for the SOP on equipment decontamination). The required QC limits of for FB concentrations are to be less than the method's RL. Composite FBs will be sampled at a frequency of one for every 20 field samples from every non-dedicated piece of sampling equipment. The results from the FBs will be assessed for bias resulting from contamination. If bias is present, the usability of the

associated analytical results will be further assessed and qualified, as appropriate. FBs will only be analyzed in the event that non-dedicated sampling equipment will be used

Matrix spikes and matrix spike duplicates (MS/MSDs) will be used to assess the effects of sample matrix interference on the precision and accuracy of analyte recovery. MS/MSD pairs will be analyzed at a frequency of one pair for every 20 samples. QA/QC precision and accuracy criteria shall be those stated in the attached SAS request forms.

Field duplicates are collected in the field from a single aliquot of sample to determine the precision and accuracy of the sampling procedures of the field team. Field duplicate will be collected and analyzed at a frequency of one duplicate for every 20 samples. The precision criteria for the duplicate samples will be $\pm$ 20 percent for aqueous samples and $\pm$30 percent for soil samples due to the heterogeneous nature of the matrix.

The laboratory accuracy and precision control limits are those specified in the laboratory's SOPs found in Appendix B to this QAPP.

2.4.2 Data Precision, Accuracy, and Completeness

Field QA/QC samples and laboratory internal QA/QC samples are collected and analyzed to assess the data's usability. SAS request forms, and the analytical SOPs, state acceptance criteria for precision and accuracy requirements for these QC samples. The QA/QC criteria for the internal laboratory QC samples that are not referenced in the SAS request forms or the appropriate analytical SOPs shall be those stated in the referenced methods. Completeness is the percentage of usable data obtained during the sampling event and its acceptance criteria is project-specific.

2.4.2.1 Precision

Precision of laboratory analysis will be assessed by comparing the analytical results between MS/MSDs. The precision of the field sampling procedures will be assessed by reviewing field duplicate sample results. The relative percent difference (%RPD) will be calculated for the duplicate samples using the following equation:

$$\%RPD = \{(S - D)/[(S + D)/2]\} \times 100$$

Where: S = First sample value (original value)

D = Second sample value (duplicate value)

As stated previously, the precision criteria for duplicate samples will be $\pm$ 20 percent for aqueous samples and $\pm$30 percent for soil samples. Sample results shall be qualified "J" as estimated in quantity when this QC limit is exceeded. The acceptable MS/MSD precision criteria are stated in the appropriate SAS request forms.

2.4.2.2 Accuracy

Accuracy of laboratory results will be assessed for compliance with the established QC criteria using the analytical results of method blanks, reagent/preparation blanks, matrix spike/matrix spike duplicate samples, and field blanks. Laboratory results accuracy will be assessed for compliance with the established QC criteria described in the SAS request forms.

The percent recovery (%R) of laboratory control samples will be calculated using the following equation:

$$\%R = (A/B) \times 100$$

Where: A = The analyte concentration determined experimentally from the laboratory control sample

B = The known amount of concentration in the sample

The accuracy criteria for the QA/QC samples are those stated in the appropriate SAS request forms.

2.4.2.3 Completeness

The data completeness of laboratory analyses results will be assessed for compliance with the amount of data required for decision-making. Complete data is data that is not rejected. Data qualified with qualifiers such as a "J" or a "UJ" are still deemed acceptable and can still be used to make project decisions. The completeness of the analytical data is calculated using the following equation:

$$\%\ \text{Completeness} = [(\text{Valid data obtained}) / (\text{Total data planned})] \times 100$$

The % completeness goal for this sampling event is 90 percent.

2.4.2.4 Representativeness

Representativeness is the degree to which sampling data accurately and precisely represent site conditions, and is dependent on sampling and analytical variability and the variability of environmental media at the site. Representativeness is a qualitative "measure" of data quality.

The goal of achieving representative data in the field starts with a properly designed and executed sampling program that carefully considers the overall DQOs for the project. Proper location controls and sample handling are critical to obtaining representative samples.

The goal of achieving representative data in the laboratory is measured by assessing accuracy and precision. A laboratory will provide representative data when all of the analytical systems are in control. Therefore, representativeness is a redundant DQO for laboratory systems if proper analytical procedures are followed and holding times are met.

In addition, laboratories must demonstrate that the staff is qualified to perform the analyses, they are certified, and they are proficient with analytical methods being employed.

2.4.2.5 Comparability

Comparability is the degree of confidence with which one data set can be compared to another. Comparability is a qualitative "measure" of data quality.

The goal of achieving comparable data in the field starts with a properly designed and executed sampling program that carefully considers the overall DQOs for the project. Proper location controls and sample handling are critical to obtaining comparable samples.

The goal of achieving comparable data in the laboratory is measured by assessing accuracy and precision. A laboratory will provide comparable data when all of the analytical systems

are in control. Therefore, comparability is a redundant DQO for laboratory systems if proper analytical procedures are followed and holding times are met.

2.4.2.6 Sensitivity

Sensitivity is defined as the ability of the method or instrument to detect the contaminant of concern and other target compounds at the level of interest. Appropriate sampling and analytical methods will be selected that have QC acceptance limits that support the achievement of established performance criteria. Assessment of sensitivity will require thorough data validation.

2.5 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Trip blanks (TB) are used to detect VOC contamination during sample shipping and handling to assess possible contamination through sample transport. The subcontracted, laboratories will provide trip blank samples to be analyzed. Trip blanks will consist of a preserved, certified clean VOC sample vial filled with contaminant-free laboratory water. The vials will contain no air bubbles. One trip blank sample will be sent for each day VOC samples are shipped to the laboratory, in each cooler containing VOC samples. Corrective action measures will be implemented if analyte concentrations are greater or equal to the specified reporting limits.

2.5.1 Field Instrument Maintenance

2.5.1.1 Equipment Monitoring

On a daily basis, the field equipment will be calibrated and checked for indications of poor performance, and the results documented. Any discrepancies will be immediately reported to the appropriate personnel for resolution.

The field team will maintain a sufficient supply of spare parts to minimize downtime. Whenever possible, backup instrumentation will be on hand.

The field equipment will be maintained as stated in the equipment's specific operating manuals. The field equipment to be used in taking field measurements includes:

- Oil/Water interface probe
- Organic vapor photoionization detector (PID)
- Oxygen, carbon dioxide, and temperature soil gas meter
- DO, temperature, pH, conductivity, and ORP meter

2.5.2 Laboratory Equipment/Instruments

Only qualified personnel will service instruments and equipment. Repairs, adjustments, and calibrations will be documented in the appropriate logbook or data sheet.

2.5.2.1 Instrument Maintenance

Preventive maintenance of laboratory equipment will follow guidelines recommended by the manufacturer. A malfunctioning instrument will be repaired by in-house staff or through a service call to the manufacturer.

The laboratory will maintain a sufficient supply of spare parts for its instruments to minimize downtime. Whenever possible, backup instrumentation will be on hand.

Whenever practical, analytical equipment should be maintained under a service contract. Such contracts allow for preventative system maintenance and repair on an "as-needed" basis. The laboratory should have sufficient trained staff to allow for the day-to-day maintenance of equipment. All laboratory instruments will be maintained in accordance with manufacturer's specifications and within the requirements of the laboratory QAM.

Preventative maintenance for the SAS analyses are described in the individual SAS requests in Appendix A. All maintenance activities are required to be documented in the log books to provide a history of maintenance records.

2.5.2.2 Equipment Monitoring

On a daily basis, operation of balances, ovens, refrigerators, and water purification systems will be checked and documented. Any discrepancies will be immediately reported to the appropriate laboratory personnel for resolution.

Specific laboratory preventative maintenance procedures are found in the laboratory's internal QAM.

2.6 Instrument Calibration and Frequency

2.6.1 Field Instruments

Calibration of field instruments, as specified by the SOPs, will be performed at the intervals specified by the manufacturer or more frequently as conditions dictate. In the event that an internally calibrated field instrument fails to meet calibration/checkout procedures, it will be replaced by the vendor and returned to the manufacturer for service.

2.6.2 Laboratory Instruments

Calibration procedures for the laboratory equipment will be as specified in the SASs. Records of calibration, repairs, or replacement will be filed and maintained by the designated laboratory personnel performing QC activities. These records will be filed at the location where the work is performed and will be subject to a QA audit.

All standards used in the calibration of equipment will be traceable, directly or indirectly, to the National Institute of Standards and Technology (NIST). All standards received will be logged into standard receipt logs maintained by the individual analytical groups. Each group maintains a standards log which tracks the preparation of standards used for calibration and QC purposes.

2.7 Inspection/Acceptance Requirements for Supplies and Consumables

It is expected that several contractors will provide various services to multiple project tasks. The required services must meet the task scope, specified levels of quality, and the submittal schedule. Project contractors or vendors should have contractual arrangements with their suppliers of materials.

2.8 Non-Direct Measurements

This subsection describes the identity of the types of data needed for project implementation and decision-making that is not obtained from direct measurements.

The project objectives are first identified, to assess what types of information are needed to implement a project plan that will meet these proposed objectives. Project objectives are summarized in Section 1 of this QAPP. Typically, the data needed to achieve the project objectives include site maps, sampling location selection and sample identifiers, laboratory method selection and detection limit verification, analytical parameter lists and critical values, field measurement lists and a project schedule. This information is included in this QAPP.

The sampling design and rationale of the LTRA sampling activities were based upon previously collected data. Site maps and other site characterization data were used in the selection of monitoring well and residential well locations. The WPDES permit specifies the sampling frequency and parameter list to be monitored at the wastewater treatment plant during the LTRA.

2.9 Data Management Plan

This DMP outlines the procedures for storing, handling, accessing, and securing data collected during this sampling event. Data gathered during this sampling event will be consolidated and compiled into a project database system that can be used to evaluate site conditions and data trends. This DMP will serve as a guide for all database users. The DMP is subject to future revision to allow the database management system to be modified as it is developed and maintained.

2.9.1 Data Types

Activities performed at the site will involve accessing a number of different types of data collected or retained for various uses. The following generally describes the overall contents of the project database, based upon the available data and data to be collected.

2.9.1.1 Historical Data

Sources of historical data for the site include information collected by the USEPA, WDNR, and CH2M HILL to characterize conditions at the site. That information includes both chemical and physical data for the site collected from previous PWP site activities.

2.9.1.2 Site Characterization Data

This QAPP identifies additional data to be collected for further characterization of the site. The data to be collected during the LTRA include:

- Groundwater/LNAPL thickness measurements
- Groundwater field parameter measurements
- Monitoring and residential well analyte concentrations
- Surface soil and subsurface soil analyte concentrations
- Soil gas characterization data
- Wastewater treatment system analyte concentrations

These data will be added to the project database as they become available. The data will include new data collected in the field and laboratory, validated by the USEPA. The source of the data will be noted in the database. Procedures for incorporating the data into the database are presented in subsequent sections of this QAPP.

2.9.2 Data Tracking and Management

Every data set received from analytical laboratories will be individually tracked. Analytical laboratory reports of chemical analysis results will all be tracked in a consistent fashion. Every data set will be assigned a unique identifier. The date of receipt, status of data validation, and status of database entry for each data set will all be tracked and recorded in the project database.

2.9.2.1 Hard Copy

Measurements made during field data collection activities will be recorded in field logbooks. Field data will be reduced and summarized, tabulated, and stored along with the field logbooks.

All raw analytical laboratory data is stored as the original hard copy. Hard copy information includes COC forms, analytical bench sheets, instrument printouts and chromatograms, certificates of analyses, and QA/QC report summaries. Validation reports will also be stored along with the hard copy reports.

2.9.2.2 Data Input Procedures

Sampling information, analytical results, applicable QA/QC data, and data validation qualifiers will be entered into a database for storage and retrieval during data evaluation and report development. The data will be electronically entered into the database from files received from the analytical laboratory. Printing data reports and manually comparing them to the hard copy deliverables from the laboratory will confirm correct data entry. Manual data entry of the historical site data will be validated by comparing a hard copy printout of the data, once entered, to the hard copy used to perform the data entry. All data entry validation procedures and results will be documented.

2.9.3 Computer Database

The computer database system utilizes a CH2M HILL Structured Query Language (SQL) combined with a macro-programming language and software tools to build menus, online forms, and report formats. The database will be based upon a relational model, in which independent tables containing fields of data can be linked through selected fields that are common to two or more tables. This database design allows inclusion of the historical data,

and allows users to effectively conduct trend analysis and generate a variety of data reports to aid in data interpretation.

The database must be protected from unauthorized access, tampering, accidental deletions or additions, and data or program loss that can result from power outages or hardware failure. The following procedures will be adopted to ensure this protection:

- The master database will be stored on the local area network (LAN) file server. Daily backups of the database will be made to ensure that the data will not be lost due to problems with the network.
- The database will be accessed through a special application developed to minimize possible database corruption by data users.

2.9.4 Documentation

Documentation of data management activities is critical because it provides:

- Hard copy record of project data management activities
- Reference information critical for database users
- Evidence that the activities have been properly planned, executed, and verified
- Continuity of data management operations when personnel changes occur

This QAPP will serve as the initial general documentation of the project data management efforts. Additional documentation will also be maintained to document specific issues, such as database structure definitions, database inventories, database maintenance, user requests, database issues and problems, and client contact.

2.9.5 Evidence File

The final evidence file will be the central repository for all documents that constitute evidence relevant to sampling and analysis activities. CH2M HILL is the custodian of the evidence file and maintains the contents of the evidence files for the project, including all relevant records, reports, logs, field notebooks, pictures, contractor reports, and data reviews in a secured, limited access area.

All records will be kept by CH2M HILL until project completion and project closeout. As necessary, records may be transferred to an offsite records storage facility. The records storage facility must provide secure, controlled-access storage of records. Records of raw analytical laboratory data, QA data, and reports will be kept by the subcontract laboratory for a minimum of 7 years.

2.9.6 Presentation of Site Characterization Data

In addition to laboratory data, other physical data will be collected during field efforts, including (but not limited to) water level and LNAPL depth measurements. This information will be stored in the project database. Other types of data elements may be added as the field investigation needs and activities evolve.

Depending on the data user needs, data presentation may consist of any of the following formats:

- Tabulated results of data summaries or raw data
- Figures showing concentration isopleths or location-specific concentrations
- Tables providing statistical evaluation results or calculation results
- Presentation tools such as ARCINFO or other similar analysis/presentation aids

SECTION 3

Assessment/Oversight

3.1 Assessments and Response Actions

Field and laboratory assessments will be performed to assess technical and procedural compliance with this QAPP. Performance and system audits are key to ensuring this compliance. The purposes of the audits are to:

- Confirm appropriate documents are properly completed and are kept current and orderly
- Ensure measurement systems are accurate
- Identify nonconformance or deficiencies and to initiate necessary corrective actions
- Verify that field and laboratory QA procedures called for in this QAPP are properly followed and executed

Project Managers and the Laboratory QA Manager are responsible for ensuring conformance with SOPs. Activities selected for audit will be evaluated against specified requirements, and the audit will include an evaluation of the method, procedures, and instructions. Documents and records will be examined as necessary to evaluate whether the QA program is effective and properly implemented. Reports and recommendations must be prepared on all audits and submitted to the QA Manager for retention in the project files.

3.1.1 Field Audits

Planning, scheduling, and conducting QA audits and surveillance are required to verify that site activities are being performed efficiently in conformance with approved plans, standards, federal and state regulatory requirements, sound scientific practices, and contractual requirements. Planned and scheduled audits may be performed to verify compliance with aspects of the QA program and to evaluate the effectiveness of the QA program.

Audits include:

- Objective examination of work areas, activities, and processes
- Review of documents and records
- Interviews with project personnel
- Review of plans and standards

Internal review of the sampling program will be conducted on a regular basis during the investigation phase by the FTL. The FTL will pay particular attention to the sampling program with respect to representativeness, comparability, and completeness of the specific measurement parameters involved.

Field documentation (e.g., COC forms, field daily sheets, log books) will be reviewed as generated, by the FTL or designee for accuracy, completeness, and compliance with QAPP requirements. The FTL will audit field sampling procedures periodically for compliance with QAPP procedures. The auditor will check that:

- Sampling protocols are being followed
- Samples are placed in proper containers
- Samples are stored and transported properly
- Field documentation is completed

3.1.1.1 Field Corrective Action

Any project team member may initiate a field corrective action process. The corrective action process consists of identifying a problem, acting to eliminate the problem, monitoring the effectiveness of the corrective action, verifying that the problem has been eliminated, and documenting the corrective action.

Corrective actions include correcting COC forms, problems associated with sample collection, packaging, shipping, field record keeping, or additional training in sampling and analysis. Additional approaches may include re-sampling or evaluating and amending sampling procedures. The FTL will summarize the problem, establish possible causes, and designate the person responsible for a corrective action. The FTL will verify that the initial action has been taken and that it appears to be effective. The FTL will follow up to verify that the problem has been resolved.

Technical staff and project personnel will be responsible for reporting suspected technical or QA nonconformances or suspected deficiencies by reporting the situation to the FTL. The FTL will be responsible for assessing suspected problems in consultation with the QA Manager and the Project Manager, and make a decision based on the potential for the situation to impact data quality. If it is determined that the situation warrants a reportable nonconformance requiring corrective action, the FTL will initiate a nonconformance report.

The FTL will be responsible for ensuring that corrective actions for non-conformances are initiated by:

- Evaluating all reported non-conformances
- Controlling additional work on nonconforming items
- Determining disposition or action to be taken
- Maintaining a log of non-conformances
- Reviewing nonconformance reports and corrective actions taken
- Ensuring nonconformance reports are included in the final documentation in the project files

3.1.2 Laboratory Audits

The Laboratory QA Manager may conduct internal system audits. An internal audit is a qualitative evaluation of all components of the laboratory QC measurement system. The audit serves to determine if all measurement systems are being used appropriately. The system audits are conducted to evaluate the following:

- Sample handling procedures
- Calibration procedures
- Analytical procedures
- QC results
- Safety procedures

- Record keeping procedures
- Timeliness of analysis and reporting.

In addition, laboratories are subject to external audits. The focus of these audits is to assess general laboratory practices and conformance to this QAPP. Laboratory audits may be performed prior to the start of analyses for this project and at any time during the course of the project as deemed necessary.

The Laboratory QA Manager will review internal laboratory performance. The Laboratory QA Manager will evaluate laboratory precision and accuracy by comparing results of duplicate samples, QC samples, spikes, and blanks. When a beyond-control-limit situation is encountered, analytical results are checked by the laboratory QA manager or other client services individual prior to distribution.

External reviews of laboratory performance may also be conducted based on evaluation of the results of check samples analyzed as part of the USEPA and/or state certification requirements. In addition, performance audits may be conducted by sending "double blind" performance evaluation (PE) samples (e.g., samples which are not discernable from routine field samples) to the analytical laboratory. External audits of the laboratory may be conducted by USEPA Region 5 or the WDNR.

3.1.2.1 Laboratory Corrective Action

Corrective actions may be required for two classes of problems: analytical/equipment problems and noncompliance problems. Analytical/equipment problems may occur during sampling, sample handling, sample preparation, laboratory instrumental analysis, or data review.

For noncompliance problems, a corrective action program will be determined and implemented at the time the problem is identified. The person who identifies the problem will be responsible for notifying the proper project member. If the problem is analytical in nature, information on these problems will be communicated to the Laboratory QA Manager and the QA Manager, who will in turn direct information to proper project members. Implementation of corrective action will be confirmed through similar channels.

Implementation of all corrective actions will be documented. No staff member will initiate corrective action without prior communication of the action needing correction and the proposed corrective action through the proper channels. If corrective actions are insufficient, the Project Manager or the QA Manager may stop work by issuing a stop-work order.

Corrective actions are required whenever an out-of-control event or potential out-of-control event is noted. The investigative action taken is somewhat dependent on the analysis and the event. Laboratory personnel are alerted that corrective actions may be necessary if:

- QC data are outside the warning or acceptable windows for precision and accuracy
- Blanks contain target analytes above acceptable levels
- Undesirable trends are detected in spike recoveries or RPD between duplicates
- Unusual changes in detection limits occur
- Inquiries concerning data quality are received
- Deficiencies are detected by the Laboratory QA Manager during internal or external audits or from results of performance evaluation samples

Corrective action procedures are often handled at the bench level by the analyst, who reviews preparation or extraction procedures for possible errors, checks instrument calibrations, spike and calibration mixes, and instrument sensitivity. If problems persist, or cannot be identified, matters are referred to the Laboratory Supervisor, Laboratory Project Manager, or Laboratory QA Manager for further investigation. Once resolved, full documentation of the corrective action procedures is filed with the Laboratory QA Manager after approval by CH2M HILL. Corrective action may include:

- Re-sampling and analyzing
- Evaluating and amending sampling procedures
- Evaluating and amending analytical procedures
- Accepting data and acknowledging the level of uncertainty
- Re-analyzing the samples, if sample or extract volume is adequate and holding time criteria permits

If resampling is deemed necessary due to laboratory problems, the Project Manager must identify the appropriate approach including cost recovery from the laboratory for the additional sampling effort.

3.2 Reports to Management

In addition to the audit reports that may be submitted to the Site Manager (SM) in accordance to this QAPP, a monthly progress report is prepared by the SM, addressing all QA issues and corrective actions proposed or already taken, and is submitted to the USEPA WAM and the WDNR. Also, after the sample results are received from the laboratory, evaluated, reduced, and tabulated, a data evaluation report will be submitted which documents the field investigation.

SECTION 4

Data Validation and Usability

4.1 Data Review, Verification, and Validation

Data validation is the process by which data generated in support of a project are reviewed against the data QA/QC requirements. The data are evaluated for precision and accuracy against the analytical protocol requirements stated in the SAS request forms. Nonconformance or deficiencies that could affect the precision or accuracy of the reported result are identified and considered when assessing whether the result is sufficient to achieve DQOs.

All data collected as part of this monitoring plan will be consistent with this QAPP. All CLP-equivalent data reports (Level 3 analyses) will be validated using the USEPA CLP National Functional Guidelines for Organic Data Review (October 1999) and Region 5 Standard Operating Procedures for Validation of CLP Organic Data (Revised February 1997) as templates. Criteria for assessment (e.g., DQOs contained in these documents) are superceded by the SAS request forms included in this QAPP.

The validation will be conducted by the USEPA. Validation of laboratory data packages will include an assessment of compliance with SAS request forms and method guidelines, specifically including an evaluation of:

- Holding times
- Blank contamination
- Calibration Requirements (initial and continuing)
- Matrix spike and duplicate recoveries
- Surrogate spike recoveries
- Instrument performance
- Compound identification and quantitation

The following steps are included as part of the data validation process:

- Evaluation of completeness of data package.
- Verification that field COC forms were completed and that the samples were handled properly.
- Verification that holding times were met for each parameter. Holding time exceedances will be documented. Data for all samples exceeding holding time requirements will be flagged as holding time exceeded. The validator on a case-by-case basis will make the decision as to which qualifiers are more appropriate.
- Verification that parameters were analyzed according to methods specified.
- Review of QA/QC data (i.e., assurance that duplicates, blanks, and spikes were analyzed on the required number of samples as specified in the method; verification that duplicate and matrix spike recoveries were acceptable).

- Investigation of anomalies identified during review. Anomalies that are identified will be discussed with the QA Manager and the Laboratory QA Manager.

Deficiencies discovered as a result of data validation, as well as corrective actions implemented in response, will be documented and submitted in the form of a written report with supporting documentation supplied as check sheets. USEPA Functional Guidelines will be used as guidance on data validation procedures. QC requirements specified in the SAS request forms shall take precedence over the Functional Guidelines requirements when listed.

4.2 Validation and Verification Methods

The data validation process is conducted to assess the effect of the overall sampling and analysis process on the usability of the data. There are two areas of review: laboratory performance evaluation, and the effect of matrix and sampling interference. Evaluation of laboratory performance is a check for compliance with the method requirements and is a straightforward examination. The laboratory either did or did not analyze the samples within the QC limits of the analytical method and according to protocol requirements. The assessment of potential matrix and sampling affects consists of a QC evaluation of the analytical results, the results of testing blank, duplicate, and matrix spike samples, and then assessing how, if at all, this could affect the usability of the data.

All analytical data will be supported by a data package. The data package will contain the supporting QC data for the associated field samples (see Section 1.7 of this QAPP for the data package content requirements). Before the laboratory will release each data package, the Laboratory QA Manager (or the analytical section supervisor) must carefully review the sample and laboratory performance QC data to verify sample identity, the completeness and accuracy of the sample and QC data, and compliance with method specifications.

The USEPA will perform data validation for laboratory-generated data in a manner consistent with USEPA's *Region 5 Standard Operating Procedures for Validation of CLP Organic Data* and USEPA's *Contract Laboratory Program National Functional Guidelines for Organic Data Review.* Sample results will then be assigned a degree of usability based upon overall data quality.

The CH2M HILL project team will evaluate the data validation results. This evaluation will assess how the data, as qualified by the data validation, can be used on the project.

The data, after validation, will also be verified to assess if the correct samples were analyzed and the correct parameters were reported. The data is also verified to assess if the EDDs and the hard copy data deliverables are consistent with one another to assure an accurate database. Also, the data will be looked at in such a way as to see if the results make sense in compared to what is anticipated. If the data is consistent with anticipated results, no corrective action will be deemed necessary. However, if the data obtained from the laboratory is not consistent with the anticipated results, a more in-depth evaluation of the results may be necessary to interpret the deviation.

4.3 Reconciliation with Data Quality Objectives

The final activity of the data validation process is to assess whether or not the data fulfilled the planned objectives for the project. The final results, as adjusted for the findings of any data

validation/data evaluation, will be checked against the DQOs. The data acquired from the additional site investigation should fulfill the following project objectives:

- Determine existing groundwater contaminant and natural attenuation parameter concentrations
- Confirm that contaminants do not extend to drinking water wells
- Provide information to assist in the operation of the groundwater treatment facility and bioventing system and monitor their performance
- Ensure compliance with WPDES Permit discharge requirements through the collection and analysis of treatment system influent and effluent samples
- Evaluate treatment system residuals and LNAPL contaminant concentrations
- Sample and analyze soil gas samples to monitor oxygen uptake and contaminant reductions in soils resulting from bioventing system operation

The data collected from the LTRA will be evaluated to assess if the above project objectives have been met. The above question will be answered assuming all scheduled samples and data readings documented in this QAPP are obtainable, and all of the data is deemed useable after sufficient validation and evaluation. If this question is not answered, future data collection will be required and implemented accordingly. If the data, after validation and evaluation, are sufficient to achieve project objectives, the data quality and project managers will release the data and work may proceed.

SECTION 5

References

CH2M HILL. *Remedial Investigation Report: Penta Wood Products Town of Daniels, Wisconsin.* Final. June 1998.

CH2M HILL. *O&M Manual: Penta Wood Products Town of Daniels, Wisconsin – Long-Term Response Action.* October 2000.

CH2M HILL. *Sampling and Analysis Plan: Penta Wood Produces Town of Daniels, Wisconsin – Long-Term Response Action.* November 2000.

USEPA. *Record of Decision: Final Remedial Action – Penta Wood Products Superfund Site Town of Daniels, Wisconsin..* September 1998.

Appendix A

Special Analytical Services

Special Analytical Service Request Forms

1. Pentachlorophenol (aqueous)
2. Total Suspended Solids (aquesous)
3. Chloride (aqueous)
4. Diesel Range Organics (aqueous)
5. Total Organic Carbon (aqueous)
6. Trimethyl benzenes + BTEX (aqueous)
7. 2,3,78-TCDD (aqueous)
8. Naphthalene + Phenol (aqueous)
9. Benzene (aqueous)
10. BTEX (aqueous)
11. Arsenic (aqueous)
12. Metals (aqueous)
13. Acid Extractables (aqueous)
14. Dioxins and Furans (aqueous)
15. Alkalinity (aqueous)
16. Nitrate (aqueous)
17. Sulfate (aqueous)
18. Sulfide (aqueous)
19. Hardness (aqueous)
20. Methane (aqueous)
21. Pentachlorophenol (soil)
22. Total Petroleum Hydrocarbons (soil)
23. Diesel Range Organics (soil)

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
PCP-Water (8151)

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham — Acting Technical Project Manager (TPO): C. Moore
C. Telephone Number: (312) 353-2310 — (312) 886-1488
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of pentachlorophenol (PCP) in aqueous samples by gas chromatography using methylation derivatization. Sample results will be reported as µg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   For each sampling round, analyze 52 low concentration water samples (1 sample weekly). This number is not inclusive of field QA/QC samples (duplicates, blanks and MS/MSD). Several additional samples will be collected during the start-up of the wastewater treatment facility.

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calendar days of receipt of samples, unless a quick turn-around-time is specified. Quick TAT samples require preliminary results in the designated time frame with a full data package to be supplied to CH2M HILL after 21 calendar days from sample receipt.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from SW846 Methods 8151 with special instructions as noted in Section 8.

   Samples will be stored at 4°C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Follow protocol according to SW-846 method 8151..

The initial calibration curve shall have 5 different levels of standards.

Dilute and reanalyze samples with analyte concentrations greater than in the highest calibration standard.

Holding time shall not exceed 7 days to sample extraction and then an additional 40 days to sample analysis.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information as designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data as specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data (including, but not limited to forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks) shall be submitted. If originals were submitted in another data package, exact copies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to CH2M HILL within the time frame listed in section 6 above. Exact copies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

5/016-6/96

I. DATA REQUIREMENTS

Parameter	Required Reporting Limits (ug/L)
PCP	0.1

II. QC REQUIREMENTS

As required by the SW846 Method 8151.

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 10 or fewer samples	concentration < reporting limit
Laboratory control sample/Laboratory Control Sample Duplicate	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
Matrix Spike/Matrix Spike Duplicate	at least one per group of 20 or fewer samples	Accuracy:± 30% Precision: ± 20%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgnt. Section
77 West Jackson, SM-5J
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
TSS - Water

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal

A. EPA Region/Client:	Region V		
B. RSCC Representative:	H. Pham	Technical Project Officer (TPO):	C. Moore
C. Telephone Number:	(312) 353-2310		(312) 886-1488
D. Date of Request:	April 2001		
E. Site Name:	Penta Wood Products – Danials, WI		

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

Analysis of total suspended solids (TSS) in aqueous samples. Sample results will be reported as mg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or Soil and sediments; and whether low, medium, or high concentrations):**

Analyze 6 aqueous samples (1 sample monthly for the first quarter, then 1 sample quarterly) for the first year, then 4 samples yearly. This number is not inclusive of QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, ETC.):**

Superfund remedial.

4. **Estimated date(s) of collection:**

April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

Method of shipment will be daily shipment by overnight carrier.

6. **Approximate number of days results required after lab receipt of samples:**

The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

Analytical protocol taken from EPA Method 160.2 with special instructions as noted in Section 8.

Samples stored at 4 C until analysis and validation results.

Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for TSS should be less than or equal to 4.0 mg/L

Follow protocol according to EPA Method 160.2.

All QA/QC requirements shall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used must be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts, and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number, and sample number.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original chain of custody forms, airbills, and any other original receiving or transmittal forms, or copies of receiving logbook pages, pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above.

Payment to laboratories for thes SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact:** Dave Shekoski
Phone: (414) 272-2426

I. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (±% or conc)
Preparation Blank	At least 1 per group of 20 or fewer samples	≤ LOQ
Lab Duplicate	At least 1 per group of 20 or fewer samples	± 20%

II. Data Requirements

Parameter	Required Detection Limits	Precision Desired
TSS	4.0 mg/L	+/- 20 percent

III. Action Required if Limits are Exceeded:

Take corrective action and resample affected samples. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgnt. Section
77 West Jackson, SM-5J
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Chloride - Water

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal

A. EPA Region/Client:	Region V		
B. RSCC Representative:	H. Pham	Technical Project Officer (TPO):	C. Moore
C. Telephone Number:	(312) 353-2310		(312) 886-1488
D. Date of Request:	September 2000		
E. Site Name:	Penta Wood Products – Danials, WI		

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

Analysis of chloride in aqueous samples. Sample results will be reported as mg/L. Samples will be unfiltered.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or Soil and sediments; and whether low, medium, or high concentrations):**

Analyze 4 aqueous (1 sample collected quarterly) each year. This number is not inclusive of QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, ETC.):**

Superfund remedial.

4. **Estimated date(s) of collection:**

April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

Method of shipment will be daily shipment by overnight carrier.

6. **Approximate number of days results required after lab receipt of samples:**

The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Analytical protocol taken from EPA Method 325.1 with special instructions as noted in Section 8.

Samples stored at 4 C until analysis and validation results.

Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

The detection limit for chloride should be less than or equal to 1.0 mg/L

Samples with chloride exceeding that of the highest calibration shall be diluted and re-analyzed.

Follow protocol according to EPA Method 325.1.

All QA/QC requirements shall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of Custody documentation, etc.). If not completed, format of results will be left to program discretion.

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used must be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts, and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number, and sample number.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original chain of custody forms, airbills, and any other original receiving or transmittal forms, or copies of receiving logbook pages, pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above.

Payment to laboratories for thes SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (±% or conc)
Preparation Blank	At least 1 per group of 20 or fewer samples	≤ LOQ
LCS/LCSD	At least 1 per group of 20 or fewer samples	Accuracy ± 20% Precision ± 20%
MS/MSD	At least 1 per group of 20 or fewer samples	Precision ± 30% Accuracy ± 30%

II. Data Requirements

Parameter	Limit of Quantification
Chloride	1.0 mg/L

III. Action Required if Limits are Exceeded:

Take corrective action and resample affected samples. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
DRO (Diesel Range Organics) in Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham Technical Project Manager (TPM): C. Moore
C. Telephone Number: (312) 353-2310 (312) 886-1488
D. Date of Request: April 2001
E. Site Name: Penta Wood Products – Daniels, Wisconsin

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of aqueous samples for Diesel Range Organics (DRO) ,$C_{10} - C_{28}$, using the Wisconsin Modified method for DRO. All samples will be reported in units of mg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 12 aqueous samples (1 sample to be collected monthly), this number is not inclusive of field QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The holding time is not to exceed 7 days from sample collection to sample extraction and 40 days from sample extraction to sample analysis.

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from the attached Wisconsin Modified Method for DRO with special instructions as noted in Section 8.

   Samples will be stored at 4°C until analysis and validation of results.

   Samples must be preserved with 5 mls of 50% HCL at the time of collection.

Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**
   a. The detection limit for DRO shall be less than or equal to 1 mg/L.. The laboratories Standard operating procedure must be supplied before the notice to proceed will be provided..
   b. Samples must be refrigerated at 4°C from the time of sample receipt until extraction, and from the time of extraction to analysis.
   c. All QA/AC requirements (Surrogates, Matrix Spike/ Matrix Spike Duplicates, Laboratory Blanks) shall be performed and reported as recommended in the method. The frequencies and acceptance criteria used shall be those specified by this SAS.
   d. Sample results that fall outside of the initial calibration concentrations must be diluted and reanalyzed.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

   All original raw data (including, but not limited to forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or external chain of custody forms, shipping documentation, strip charts and copies of pages from preparation and analysis logbooks) shall be submitted. If originals were submitted in another data package, exact copies may be submitted with a record of the location of the originals.

   All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

10. **Other (use additional sheets or attach supplementary information, as needed):**

    The laboratory shall provide their most recent MDL study using the specified protocol before being provided a notice to proceed.. The laboratory shall adhere to chain-of-custody and document control procedures as specified in the most recent CLP SOW.

    Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
    David Shekoski (414)272-2426

5/016-6/96

I. DATA REQUIREMENTS

Analyte	MDL (mg/L)
Total Diesel Range Organics (DRO)	1.0

II. QC REQUIREMENTS

As required by the attached Wisconsin Modified Method for DRO

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgnt. Section
77 West Jackson, SM-5J
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
TOC - Water

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal

A. EPA Region/Client:	Region V		
B. RSCC Representative:	H. Pham	Technical Project Officer (TPO):	C. Moore
C. Telephone Number:	(312) 353-2310		(312) 886-1488
D. Date of Request:	April 2001		
E. Site Name:	Penta Wood Products – Danials, WI		

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

Analysis of total organic carbon (TOC) in aqueous samples. Sample results will be reported as mg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or Soil and sediments; and whether low, medium, or high concentrations):**

Analyze 12 aqueous samples (1 sample to be collected monthly). This number is not inclusive of QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, ETC.):**

Superfund remedial.

4. **Estimated date(s) of collection:**

April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

Method of shipment will be daily shipment by overnight carrier.

6. **Approximate number of days results required after lab receipt of samples:**

The laboratory will be required to provide results within 21 calendar days of receipt of samples..

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

Analytical protocol taken from SW-846 9060 with special instructions as noted in Section 8.

Samples will be preserved in the field with H_2SO_4 to a pH<2 and stored at 4°C until analysis and validation of the results

Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for TOC should be less than or equal to 1.0 mg/L

Samples with TOC exceeding that of the highest calibration shall be diluted and re-analyzed.

Follow protocol according to SW-846 Method 9060.

All QA/QC requirements shall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used must be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts, and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number, and sample number.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original chain of custody forms, airbills, and any other original receiving or transmittal forms, or copies of receiving logbook pages, pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above.

Payment to laboratories for thes SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (±% or conc)
Preparation Blank	At least 1 per group of 20 or fewer samples	≤ LOQ
LCS/LCSD	At least 1 per group of 20 or fewer samples	Accuracy ± 20% Precision ± 20%.
MS/MSD	At least 1 per group of 20 or fewer samples	Accuracy ± 30% Precision ± 30%

II. Data Requirements

Parameter	Required Detection Limits
TOC	1.0 mg/L

III. Action Required if Limits are Exceeded:

Take corrective action and resample affected samples. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Trimethylbenzenes +
BTEX-Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham — Acting Technical Project Manager (TPO): C. Moore
C. Telephone Number: (312) 353-2310 — (312) 886-1488
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of volatile organic compounds (VOCs) in aqueous samples using gas chromatography/mass spectrometry (GC/MS). Sample results will be reported as µg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   For each sampling round, analyze 6 low concentration water samples (1 sample monthly for the first quarter then 1 sample quarterly). This number is not inclusive of field QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calandar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from SW846 Methods 5030/8260 with special instructions as noted in Section 8.

   Samples will be preserved in the field with HCl to pH<2, and stored at 4°C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Follow protocol according to SW-846 method 8260.

The initial calibration curve shall have 5 different levels of standards.

Dilute and reanalyze samples with analyte concentrations greater than in the highest calibration standard.

Holding time shall not exceed 14 days from sample collection

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information as designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data as specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data (including, but not limited to forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks) shall be submitted. If originals were submitted in another data package, exact copies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to CH2M HILL within the time frame listed in section 6 above. Exact copies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

5/016-6/96

I. DATA REQUIREMENTS

Parameter	Required Reporting Limits (ug/L)
Benzene	0.5
Toluene	5.0
Xylene(s)	5.0
Ethylbenzene	5.0
1,3,5-trimethylbenzene	5.0
1,2,4-trimethylbenzene	5.0
Total trimethylbenzene	10.0

II. QC REQUIREMENTS

As required by the SW846 Method 8260.

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 10 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Dioxins (2,3,7,8-TCDD)

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 886-1488
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Acting Technical Project Manager (TPO): C. Moore
(312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of 2,3,7,8-TCDD in aqueous samples by SW-846 Method 8290

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   For each sampling round, analyze 12 aqueous samples (1 sample collected monthly). This number is not inclusive of field QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from SW846 Method 8290 with special instructions as noted in Section 8.

   Samples will be stored at 4°C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Follow protocol according to SW-846 method 8290.

The initial calibration curve shall have 5 different levels of standards.

Dilute and reanalyze samples with analyte concentrations greater than in the highest calibration standard.

Holding time shall not exceed 30 days to extraction and 45 days to analysis from the date of sample extraction.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.

The laboratory shall perform data reduction and shall report sample analysis data and quality control information as designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data as specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data (including, but not limited to forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks) shall be submitted. If originals were submitted in another data package, exact copies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. Other (use additional sheets or attach supplementary information, as needed):

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to CH2M HILL within the time frame listed in section 6 above. Exact copies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. Name of sampling/shipping contact and phone number:
David Shekoski (414)272-2426

5/016-6/96

I. DATA REQUIREMENTS

Parameter	Required Reporting Limits (ug/L)
2,3,7,8-TCDD	0.000003

II. QC REQUIREMENTS

As required by the SW846 Method 8290

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 10 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Naphthalene and Phenol -Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham — Acting Technical Project Manager (TPO): C. Moore
C. Telephone Number: (312) 353-2310 — (312) 886-1488
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of naphthalene and phenol in aqueous samples using gas chromatography/mass spectrometry (GC/MS). Sample results will be reported as µg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   For each sampling round, analyze 12 low concentration water samples (1 sample collected monthly). This number is not inclusive of field QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from SW846 Methods 8270 with special instructions as noted in Section 8.

   Samples will be stored at 4°C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Follow protocol according to SW-846 method 8270.

The initial calibration curve shall have 5 different levels of standards.

Dilute and reanalyze samples with analyte concentrations greater than in the highest calibration standard.

Holding time shall not exceed 7 days to sample extraction and then an additional 40 days to sample analysis.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information as designated in the CLP SOW, Rev. 8/94. The sample analysis data package shall include all documentation, data reporting forms and raw data as specified in CLP SOW, Rev. 8/94.

All procedures used shall be clearly identified. All original raw data (including, but not limited to forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks) shall be submitted. If originals were submitted in another data package, exact copies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to CH2M HILL within the time frame listed in section 6 above. Exact copies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

5/016-6/96

I. DATA REQUIREMENTS

Parameter	Required Reporting Limits (ug/L)
Naphthalene	5.0
Phenol (total)	5.0

II. QC REQUIREMENTS

As required by the SW846 Method 8260A.

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 10 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Benzene-Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham Acting Technical Project Manager (TPO): C. Moore
C. Telephone Number: (312) 353-2310 (312) 886-1488
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of volatile organic compounds (VOCs) in aqueous samples using gas chromatography/mass spectrometry (GC/MS). Sample results will be reported as µg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   For each sampling round, analyze 6 low concentration water samples (1 sample monthly for the first quarter then 1 sample quarterly). This number is not inclusive of field QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from SW846 Methods 5030/8260 with special instructions as noted in Section 8.

   Samples will be preserved in the field with HCl to pH<2, and stored at 4°C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Follow protocol according to SW-846 method 8260.

The initial calibration curve shall have 5 different levels of standards.

Dilute and reanalyze samples with analyte concentrations greater than in the highest calibration standard.

Holding time shall not exceed 14 days from sample collection

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information as designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data as specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data (including, but not limited to forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks) shall be submitted. If originals were submitted in another data package, exact copies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to CH2M HILL within the time frame listed in section 6 above. Exact copies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

5/016-6/96

I. DATA REQUIREMENTS

Parameter	Required Reporting Limits (ug/L)
Benzene	0.5

II. QC REQUIREMENTS

As required by the SW846 Method 8260.

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 20 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
BTEX- Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 353-2310
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Technical Project Manager (TPO): C. Moore
312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of benzene, toluene, ethylbenzene, and total xylenes (BTEX) in groundwater samples using gas chromatography/mass spectrometry (GC/MS). Sample results will be reported as µg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 48 groundwater samples This number is not inclusive of field QA/QC samples (duplicates, blanks) and laboratory QC (MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The holding time is not to exceed 14 days from sample collection.

   The laboratory will be required to provide results within 21calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from SW846 Method 8260 with special instructions as noted in Section 8.

   Samples will be preserved in the field with HCl to pH<2 and stored at 4 C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for benzene shall be less than or equal to 0.1 µg/L. The detection limits for toluene, ethylbenzene, and xylenes shall be less than or equal to 5.0 µg/L. The most recent MDL study shall be enclosed.

The method recommended surrogate and internal standards shall be used and prepared at the recommended concentrations.

Use five calibration standards. The lowest standards should represent analyze concentrations near, but above, the respective method detection limit.

All QA/QC requirements (surrogates, matrix spike/matrix spike duplicates, lab blanks, GC/MS tuning) shall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the CLP SOW, Rev. 10/92. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in CLP SOW, Rev. 10/92.

All procedures used shall be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

The laboratory is to conduct matrix spike and matrix spike duplicate (MS/MSD) analyses and report the results on the appropriate form.

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above. Photocopies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

I. **DATA REQUIREMENTS**

Parameter	Required Detection Limits
Benzene	0.1 µg/L
Toluene	5.0 µg/L
Ethylbenzene	5.0 µg/L
Xylenes (total)	5.0 µg/L

II. QC REQUIREMENTS

As required by the SW846 Method 8260.

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 10 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact the Region for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Arsenic-Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 353-2310
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Technical Project Manager (TPO): C. Moore
(312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of arsenic in water samples. Sample results will be reported in µg/L

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 101 groundwater samples. This number is not inclusive of QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from SW846 Method 6010/7060 with special instructions as noted in Section 8.

   Samples will be preserved in the field with HNO_3 to pH<2, and stored at 4 C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for arsenic shall be less than or equal to 2.0 µg/L. The most recent MDL study shall be enclosed.

Follow protocol according to the SW846 Method 6010/7060. Dilute samples with sample concentrations greater than the highest standard.

All QA/QC requirements shall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

The laboratory is to conduct matrix spike and matrix spike duplicate (MS/MSD) analyses and report the results on the appropriate form.

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above. Photocopies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

I. DATA REQUIREMENTS

Parameter	Required Detection Limits
Arsenic	1.0 µg/L

II. QC REQUIREMENTS

As required by the SW846 Method 6010/7060.

Audits Required	Frequency of Audits	Limits* (±% or conc)
Preparation Blank	At least 1 per group of 10 or fewer samples	Concentration < RL
LCS/LCSD	At least 1 per group of 20 or fewer samples	Accuracy: +- 20% Precision: +- 20%
MS/MSD	At least 1 per group of 20 or fewer samples	Accuracy: +- 30% Precision: +- 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact the Region for problems that might result in the delay of reporting sample results.

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgnt. Section
77 West Jackson, SM-5J
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Metals - Water

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal

A. EPA Region/Client:	Region V		
B. RSCC Representative:	H.Pham	Technical Project Officier (TPO):	C. Moore
C. Telephone Number:	(312) 353-2310		(312) 886-1488
D. Date of Request:	April 2001		
E. Site Name:	Penta Wood Products		

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

Analysis of ground water for the Attachment 1 metals with detection and reporting limits as specified in Attachment 1.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or Soil and sediments; and whether low, medium, or high concentrations):**

6 aqueous samples will be collected (monthly for the first quarter then quarterly). These samples will be analyzed for medium to low concentrations of total metals. The projected number is not inclusive of QA samples.

3. **Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, ETC.):**

Superfund remedial.

4. **Estimated date(s) of collection:**

April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

Method of shipment will be daily shipment by overnight carrier.

6. **Approximate number of days results required after lab receipt of samples:**

Samples must be extracted and analyzed within 180 days for all other metals.

The analytical results are due 21 calendar days of sample collection, the data packages are also due within 21 calendar days of sample collection.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Method SW846 6010/7000 series for the analysis of the samples with modifications noted in Section 8.

Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

1. One liter of the aqueous sample will be collected and preserved with 5 ml of HNO_3 to a pH <2. Samples should be stored at 4°C until the time of analysis.

2. Any remaining sample should be stored at 4°C until the validation and the acceptance of the sample result.

3. The RL must be shown to have been met prior to the analysis of any samples.

4. Each calibration blank and QC audit solution must contain the same nitric acid concentration as the samples, or diluted samples.

5. The sample solutions analyzed must have their matrix concentration fully documented in the raw data.

6. Each analytical determination must have the resulting absorbance clearly recorded and documented in their order of determination.

7. The calibration range of the ICP analyses can not be exceeded. Dilute any sample that does exceed the calibration range.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of Custody documentation, etc.). If not completed, format of results will be left to program discretion.

All procedures used must be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts, and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number, and sample number.

10. **Other (use additional sheets or attach supplementary information, as needed):** All original chain of custody forms, airbills, and any other original receiving or transmittal forms, or copies of receiving logbook pages, pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above.

11. **Name of sampling/shipping contact:** Dave Shekoski
Phone: (414) 272-2426

I. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (±% or conc)
Preparation Blank	At least 1 per group of 10 or fewer samples	Concentration < RL
LCS/LCSD	At least 1 per group of 20 or fewer samples	Accuracy: +- 20% Precision: +- 20%
MS/MSD	At least 1 per group of 20 or fewer samples	Accuracy: +- 30% Precision: +- 30%

III. Action Required if Limits are Exceeded:

Take corrective action and resample affected samples. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

ATTACHMENT I

	Reportin Limit (µg/L)
Arsenic	1.0
Copper	25
Iron	25
Manganese	15
Zinc	25

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Acid extractables-Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham Acting Technical Project Manager (TPO): C. Moore
C. Telephone Number: (312) 353-2310 (312) 886-1488
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of acid extractable compounds by EPA Method 625 in aqueous samples. Sample results will be reported as µg/L.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   For each sampling round, analyze 1 water samples collected annually. This number is not inclusive of field QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from EPA Method 625 with special instructions as noted in Section 8.

   Samples will be stored at 4°C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Follow protocol according to EPA Method 625.

The initial calibration curve shall have 5 different levels of standards.

Dilute and reanalyze samples with analyte concentrations greater than in the highest calibration standard.

Holding time shall not exceed 7 days to sample extraction and then an additional 40 days to sample analysis.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information as designated in the CLP SOW, Rev. 8/94. The sample analysis data package shall include all documentation, data reporting forms and raw data as specified in CLP SOW, Rev. 8/94.

All procedures used shall be clearly identified. All original raw data (including, but not limited to forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks) shall be submitted. If originals were submitted in another data package, exact copies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to CH2M HILL within the time frame listed in section 6 above. Exact copies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

5/016-6/96

I. DATA REQUIREMENTS

Parameter	Required Reporting Limits (ug/L)
4-chloro-3-methylphenol	3.0
2-chlorophenol	4.0
2,4-dichlorophenol	3.0
2,4-dimethylphenol	3.0
2,4-dinitrophenol	43.0
2-methyl-4,6-dinitrophenol	25.0
2-nitrophenol	4.0
4-nitrophenol	3.0
pentachlorophenol	4.0
phenol	3.0
2,4,6-trichlorophenol	3.0

II. QC REQUIREMENTS

As required by the SW846 Method 8260A.

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 10 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Dioxins and Furans

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham — Acting Technical Project Manager (TPO): C. Moore
C. Telephone Number: (312) 353-2310 — (312) 886-1488
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of Dioxins and Furans in aqueous samples by SW-846 Method 8290

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   For each sampling round, analyze 1 aqueous sample collected annually. This number is not inclusive of field QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from SW846 Method 8290 with special instructions as noted in Section 8.

   Samples will be stored at 4°C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Follow protocol according to SW-846 method 8290.

The initial calibration curve shall have 5 different levels of standards.

Dilute and reanalyze samples with analyte concentrations greater than in the highest calibration standard.

Holding time shall not exceed 30 days to extraction and 45 days to analysis from the date of sample extraction.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information as designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data as specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data (including, but not limited to forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks) shall be submitted. If originals were submitted in another data package, exact copies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to CH2M HILL within the time frame listed in section 6 above. Exact copies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

5/016-6/96

I. DATA REQUIREMENTS

Parameter	Required Reporting Limits (ug/L)
Total TCDD	0.0063
Total TCDF	0.0063
Total PeCDD	0.0063
Total PeCDF	0.0035
Total HeCCD	0.0063
Total HeCCF	0.0063

II. QC REQUIREMENTS

As required by the SW846 Method 8290

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 10 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Alkalinity- Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 353-2310
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Technical Project Manager (TPO): C. Moore
(312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of alkalinity in groundwater samples. Sample results will be reported as mg/L. Samples will be unfiltered.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 48 groundwater samples. This number is not inclusive of field QA/QC samples (duplicates, blanks) and laboratory QC (MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The holding time is not to exceed 14 days from sample collection.

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from EPA Method 310.1 with special instructions as noted in Section 8.

   Samples stored at 4 C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for alkalinity shall be less than or equal to 5 mg/L.

Follow protocol according to the EPA Method 310.1.

Standardize the pH meter and titrant daily. Standardize the pH meter using at least 2 buffers which bracket the pH end point.

Analyze a check standard after every 10 samples to demonstrate pH meter stability.

All QA/QC requirementsshall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in mg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above. Photocopies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

I. DATA REQUIREMENTS

Parameter	Required Reporting Limit
Alkalinity	5 mg/L

II. QC REQUIREMENTS

As required by the EPA Method 310.1.

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 20 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact the Region for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Nitrate- Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 353-2310
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Technical Project Manager (TPO): C. Moore
(312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of nitrate in groundwater samples. Sample results will be reported as µg/L. Samples will be unfiltered.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 48 low concentration groundwater samples. This number is not inclusive of field QA/QC samples (duplicates, blanks) and laboratory QC (MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calendar days of receipt of samples. Samples shall be analyzed within 48 hours of sample collection.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from EPA Method 353.2 with special instructions as noted in Section 8.

   Samples stored at 4 C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for nitrate shall be less than or equal to 1 mg/L.

Follow protocol according to the EPA Method 353.2.

All QA/QC requirementsshall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in mg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above. Photocopies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

I. DATA REQUIREMENTS

Parameter	Required Detection Limits
Nitrate	1 mg/L

II. QC REQUIREMENTS

As required by the EPA Method 353.2.

Audits Required	Frequency of Audits	Limits* (±% or conc)
Preparation Blank	At least 1 per group of 10 or fewer samples	Concentration < RL
LCS/LCSD	At least 1 per group of 20 or fewer samples	Accuracy: +- 20% Precision: +- 20%
MS/MSD	At least 1 per group of 20 or fewer samples	Accuracy: +- 30% Precision: +- 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact the Region for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Sulfate- Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 353-2310
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Technical Project Manager (TPO): C. Moore
(312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of sulfate in groundwater samples. Sample results will be reported as mg/L. Samples will be unfiltered.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 48 low concentration groundwater samples. This number is not inclusive of field QA/QC samples (duplicates, blanks) and laboratory QC (MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from EPA Method 375.1 with special instructions as noted in Section 8.

   Samples stored at 4 C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for sulfate shall be less than or equal to 10 mg/L.

Sulfate standards shall be prepared daily from stock solutions.

Samples with sulfate exceeding that of the highest calibration standard shall be diluted and re-analyzed.

Follow protocol according to the EPA Method 375.1.

All QA/QC requirementsshall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in mg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above. Photocopies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

I. DATA REQUIREMENTS

Parameter	Required Detection Limits
Sulfate	10 mg/L

II. QC REQUIREMENTS

As required by the EPA Method 375.1.

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 20 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact the Region for problems that might result in the delay of reporting sample results.

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgnt. Section
77 West Jackson, SM-5J
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Sulfide - Water

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal

A. EPA Region/Client:	Region V		
B. RSCC Representative:	H. Pham	Technical Project Officer (TPO):	C. Moore
C. Telephone Number:	(312) 353-2310		(312) 886-1488
D. Date of Request:	April 2001		
E. Site Name:	Penta Wood Products – Danials, WI		

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

Analysis of sulfide in groundwater samples. Sample results will be reported as mg/L. Samples will be unfiltered.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or Soil and sediments; and whether low, medium, or high concentrations):**

Analyze 48 low concentration groundwater samples. This number is not inclusive of field QA/QC samples (duplicates, blanks) and laboratory QC (MS/MSD).

3. **Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, ETC.):**

Superfund remedial.

4. **Estimated date(s) of collection:**

April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

Method of shipment will be daily shipment by overnight carrier.

6. **Approximate number of days results required after lab receipt of samples:**

The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Analytical protocol taken from EPA Method 376.1 with special instructions as noted in Section 8.

Samples stored at 4 C until analysis and validation results.

Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

The detection limit for sulfide should be less than or equal to 1.0 mg/L

Sulfide standards shall be prepared daily from stock solutions.

Samples with sulfate exceeding that of the highest calibration shall be diluted and re-analyzed.

Follow protocol according to EPA Method 376.1.

All QA/QC requirements shall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of Custody documentation, etc.). If not completed, format of results will be left to program discretion.

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used must be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts, and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number, and sample number.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original chain of custody forms, airbills, and any other original receiving or transmittal forms, or copies of receiving logbook pages, pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above.

Payment to laboratories for thes SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. Name of sampling/shipping contact: Dave Shekoski
Phone: (414) 272-2426

I. QUALITY CONTROL REQUIREMENTS

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 20 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

II. Data Requirements

Parameter	Required Detection Limits
Sulfide	1.0 mg/L

III. Action Required if Limits are Exceeded:

Take corrective action and resample affected samples. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Hardness-Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 353-2310
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Technical Project Manager (TPO): C. Moore
(312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of hardness in surface water samples. Sample results will be reported in µg/L as $CaCO_3$.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 48 water samples. This number is not inclusive of field QA/QC samples (duplicates, blanks) and laboratory QC (MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from EPA Method 130.1 with special instructions as noted in Section 8.

   Samples will be preserved in the field with HNO_3 to pH<2, and stored at 4 C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for hardness shall be less than or equal to 500 µg/L.

Follow protocol according to the EPA Method 130.1.

All QA/QC requirements shall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. Other (use additional sheets or attach supplementary information, as needed):

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above. Photocopies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. Name of sampling/shipping contact and phone number:
David Shekoski (414)272-2426

I. DATA REQUIREMENTS

Parameter	Required Detection Limits
Hardness	500 µg/L

II. QC REQUIREMENTS

As required by the EPA Method 130.1.

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 20 or fewer samples	concentration < reporting limit

LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact the Region for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
Methane- Water

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 353-2310
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Technical Project Manager (TPO): C. Moore
(312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of methane in groundwater samples using gas chromatography. Sample results will be reported as µg/L. Low detection limits are required.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 48 low concentration water samples. This number is not inclusive of field QA/QC samples (duplicates, blanks) and laboratory QC (MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The holding time is not to exceed 14 days from sample collection.

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from RSK 175 with special instructions as noted in Section 8.

   Samples will be stored at 4 C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for methane shall be less than or equal to 10 µg/L. The most recent MDL study shall be enclosed.

The method recommended surrogate and internal standards shall be used and prepared at the recommended concentrations.

Use five calibration standards. The lowest standards should represent analyze concentrations near, but above, the respective method detection limit.

All QA/QC requirements (surrogates, matrix spike/matrix spike duplicates, lab blanks) shall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in µg/L.

10. **Other (use additional sheets or attach supplementary information, as needed):**

The laboratory is to conduct matrix spike and matrix spike duplicate (MS/MSD) analyses and report the results on the appropriate form.

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above. Photocopies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

I. **DATA REQUIREMENTS**

Parameter	Required Detection Limits
Methane	10 µg/L

II. QC REQUIREMENTS

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 20 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact the Region for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
PCP- Soil

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 353-2310
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Technical Project Manager (TPO): C. Moore
(312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of pentachlorophenol in soil samples using gas chromatography/mass spectrometry (GC/MS). Sample results will be reported as mg/kg. Low detection limits are required.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 23 soil samples. This number is not inclusive of QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The holding time is not to exceed 7 days from sample collection to extraction and 40 days from extraction to analysis.

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from SW846 Method 8270 with special instructions as noted in Section 8.

   Samples stored at 4 C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for Pentachlorophenol shall be less than or equal to 0.5 mg/kg. The most recent MDL study shall be enclosed.

The method recommended surrogate and internal standards shall be used and prepared at the recommended concentrations.

Use five calibration standards. The lowest standards should represent analyze concentrations near, but above, the respective method detection limit.

All QA/QC requirements (surrogates, matrix spike/matrix spike duplicates, lab blanks, GC/MS tuning) shall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in mg/kg.

10. **Other (use additional sheets or attach supplementary information, as needed):**

The laboratory is to conduct matrix spike and matrix spike duplicate (MS/MSD) analyses and report the results on the appropriate form.

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above. Photocopies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

I. **DATA REQUIREMENTS**

Parameter	Required Detection Limits
Pentachlorophenol	0.5 mg/kg

II. QC REQUIREMENTS

As required by the SW846 Method 8270.

Audit	Frequency of Audits	Limits
Method Blank	at least one per group of 20 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact the Region for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
TPH- Soil

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 353-2310
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Technical Project Manager (TPO): C. Moore
(312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of total petroleum hydrocarbons (TPH) in soil samples using infrared (IR) spectrometry. Sample results will be reported as mg/kg.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 23 soil samples. This number is not inclusive of QA/QC samples (duplicates, blanks and MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The holding time is not to exceed 14 days from sample collection.

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from USEPA Method 418.1 with special instructions as noted in Section 8.

   Samples stored at 4 C until analysis and validation of results.

   Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

The detection limit for TPH shall be less than or equal to 10 mg/kg. The contract laboratories most recent MDL study shall be enclosed with the response to the request for proposal.

All QA/QC requirements shall be performed and reported as recommended in the method. The procedures, frequencies and acceptance criteria used shall be the same as those recommended in the method or referenced in the method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The laboratory shall perform data reduction and shall report sample analysis data and quality control information similar to that designated in the most recent CLP SOW. The sample analysis data package shall include all documentation, data reporting forms and raw data similar to those specified in the most recent CLP SOW.

All procedures used shall be clearly identified. All original raw data, forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or extract chain of custody forms, strip charts and copies of pages from preparation and analysis logbooks shall be submitted. If originals were submitted in another data package, photocopies may be submitted with a record of the location of the originals.

All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

Results will be reported in mg/kg.

10. **Other (use additional sheets or attach supplementary information, as needed):**

All original sample tags, chain of custody forms, SAS packing lists, airbills and any other original receiving or transmittal forms or copies of receiving logbook pages pertaining to this SAS shall be submitted to the Region within the time frame listed in section 6 above. Photocopies may be submitted with a record of the location of the originals.

Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
David Shekoski (414)272-2426

I. **DATA REQUIREMENTS**

Parameter	Required Detection Limits	Precision Desired
TPH	10 mg/kg	within historic acceptance limits

II. **QC REQUIREMENTS**

As required by the USEPA Method 418.1.

Audit	Frequency of Audits	Limits

5/016-6/96

Method Blank	at least one per group of 20 or fewer samples	concentration < reporting limit
LCS/LCSD	at least one per group of 20 or fewer samples	Accuracy: ± 20% Precision: ± 20%
MS/MSD	at least one per group of 20 or fewer samples	Accuracy: ± 30% Precision: ± 30%

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact the Region for problems that might result in the delay of reporting sample results.

5/016-6/96

U.S. Environmental Protection Agency Region V
SFD/Contracts Mgmt. Section
77 West Jackson, SM-5J
Chicago, Illinois 60604
PHONE: (312) 886-1488 FAX: (312) 886-0753

SAS Number
DRO (Diesel Range Organics) in Soil

SPECIAL ANALYTICAL SERVICES
Client Request

[X] Regional Transmittal

A. EPA Region/Client: Region V
B. RSCC Representative: H. Pham
C. Telephone Number: (312) 353-2310
D. Date of Request: April 2001
E. Site Name: Penta Wood Products

Technical Project Manager (TPM): C. Moore
(312) 886-1488

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delays in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**

   Analysis of aqueous samples for Diesel Range Organics (DRO) ,$C_{10} - C_{28}$, using the Wisconsin Modified method for DRO. All samples will be reported in units of mg/kg.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   Analyze 12 soil samples (1 sample to be collected monthly), this number is not inclusive of field QA/QC samples (duplicates, blanks) or laboratory QA/QC samples (MS/MSD).

3. **Purposes of analysis (specify whether Superfund [Remedial or Enforcement], RCRA, NPDES, etc.):**

   Superfund-Remedial

4. **Estimated date(s) of collection:**

   April 2001 through September 2003

5. **Estimated date(s) and method of shipment:**

   Method of shipment will be by overnight carrier.

6. **Number of days analysis and data required after laboratory receipt of samples:**

   The holding time is not to exceed 14 days from sample collection to sample extraction and 40 days from sample extraction to sample analysis.

   The laboratory will be required to provide results within 21 calendar days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

   Analytical protocol taken from the attached Wisconsin Modified Method for DRO with special instructions as noted in Section 8.

   Samples will be stored at 4°C until analysis and validation of results.

Note: Laboratory data rejection and non-payment will be recommended if methods other than those specified in this document are used.

8. **Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**
   a. The detection limit for DRO shall be less than or equal to 1 mg/kg.. The laboratories Standard operating procedure must be supplied before the notice to proceed will be provided..
   b. Samples must be refrigerated at 4°C from the time of sample receipt until extraction, and from the time of extraction to analysis.
   c. All QA/AC requirements (Surrogates, Matrix Spike/ Matrix Spike Duplicates, Laboratory Blanks) shall be performed and reported as recommended in the method. The frequencies and acceptance criteria used shall be those specified by this SAS.
   d. Sample results that fall outside of the initial calibration concentrations must be diluted and reanalyzed.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

   All original raw data (including, but not limited to forms, calculation worksheets, instrument read-outs, preparation forms, internal sample and/or external chain of custody forms, shipping documentation, strip charts and copies of pages from preparation and analysis logbooks) shall be submitted. If originals were submitted in another data package, exact copies may be submitted with a record of the location of the originals.

   All records of analysis and calculations shall be legible and be sufficient to recalculate all sample concentrations and QA audit results. QC reference samples or initial calibration standards shall be identified as to source, lot number and sample number.

10. **Other (use additional sheets or attach supplementary information, as needed):**

    The laboratory shall provide their most recent MDL study using the specified protocol before being provided a notice to proceed.. The laboratory shall adhere to chain-of-custody and document control procedures as specified in the most recent CLP SOW.

    Payment to laboratories for this SAS analysis may be reduced if all procedures noted above are not followed and all required deliverables noted above are not supplied. The Region or its contractors shall not be charged further for the provision of required deliverables within this agreement.

11. **Name of sampling/shipping contact and phone number:**
    David Shekoski (414)272-2426

5/016-6/96

I. DATA REQUIREMENTS

Analyte	MDL (mg/kg)
Total Diesel Range Organics (DRO)	1.0

II. QC REQUIREMENTS

As required by the attached Wisconsin Modified Method for DRO

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action. Contact CH2M HILL for problems that might result in the delay of reporting sample results.

Appendix B

Analytical Standard Operating Procedures

Analytical SOPs

1. Initial Receipt, Inventory, Preservation Verification, Labeling, and Storage
2. Internal Chain of Custody
3. Corrective Action System
4. Digestion of Liquid and Solid Samples for Cations Analyses
5. SW-846 Herbicides Extraction for Method 8151/EPA 615
6. SW-846 3510C Seperatory Funnel Extraction
7. SW-846 3550B Sonication
8. 625/8270C GC/MS Semi-Volatile Organics
9. TOC Method 415.1/9060 (total organic carbon, liquid and solid)
10. Metals by GFAA (Graphite Furnace Atomic Absorption)
11. GC/MS Volatile Organics (SW-846 8260B/EPA 624)
12. Cations by ICP (EPA 200.7, 6010B, AFCEE 3.0, and CLP ILM04.0)
13. Chlorophenoxy Acid Herbicides by Capillary Gas Chromatograpy (SW-846 8151)
14. Sample Analysis: Chloride Method 325.2 (Colormetric, Automated Ferricyanide)
15. Nitrogen, Nitrate Method 353.2 (Colormetric, Automated, Cadmium Reduction)
16. Sulfate, Method EPA 375.4 (Turbidimetric)
17. Titration Procedures for Sulfides
18. TSS Method EPA 160.2
19. Aqueous and Soil Samples for Diesel Range Organics by GC by Method 8015 Modified
20. Analysis of Dissolved Gases in Water
21. Extraction of PCDD/PCDF from Water for Methods 1613, 8290, and 551
22. PCDDs and PCDFs by HRGC/HRMS

PEL Laboratories, Inc. - Standard Operating Procedure

Sample Management: Initial Receipt, Inventory, Preservation Verification, Labeling and Storage

APPROVED:

Team Leader / Sample Custody Date

QA Officer Date

Laboratory Manager Date

SCOPE AND APPLICATION

A sample is physical evidence collected from a facility or from the environment. Controlling evidence is an essential part of any hazardous waste investigation effort.

PEL Laboratories, Inc. maintains a Sample Custody section that is responsible for verifying that samples and associated documentation are in proper order when received by the laboratory. Any discrepancies are noted by the Custody section and acted on by the Project Management Department.

The Team Leader of the Sample Custody Department is the Sample Custodian for PEL Laboratories, Inc. All staff in the Custody section (Sample Coordinators) are designated to perform the functions of the Sample Custodian as his designees.

This standard operating procedure describes the steps followed by the Sample Custody section when samples are received in the laboratory.

QA/QC REQUIREMENTS

Not applicable

EQUIPMENT/SUPPLIES

- pH indicator strips
- Polystyrene Beaker cups
- Infrared Thermometer
- Hg Thermometers

PROCEDURE

1. Samples arrive in the laboratory via courier or they are delivered by the client. Documentation is signed in order for the samples to be relinquished to the lab from the client or courier.
2. The sample coordinator writes all exceptions on the project specific COC (Figure 1), and notifies the client of any problems observed during sample receipt.
3. Initial check of samples and documentation
   a. Remove and set aside the shipping documents.
   b. Place the shipping container in a well-ventilated area and open, preferably under a canopy or inside a fume hood.
   c. Remove the COC, which should be in a waterproof bag inside the shipping container. Record the presence/absence of the COC.
   d. If there is no COC or if it is improperly filled out, the sample coordinator corrects it or creates a COC in consultation with the Project Management Department and the client. Creating a COC in this manner is not documentary proof of legal chain of custody.
   e. Carrier and air bill or other tracking number in shipping documentation is noted on the COC.

f. Verify that the COC is properly filled out. This should include the following:
   i. The project number (PEL)
   ii. Name of the project manager or client contact
   iii. Sample date
   iv. Sample matrix
   v. Signatures of both the sampler, and the person who relinquished the samples and the appropriate times and dates
   vi. All entries on the COC must be made in ink.

h. Remove the samples from the shipping container and organize them according to the client sample identifiers and by the tests required.

i. Verify the integrity and condition of all sample containers. Look for leakage, broken containers, contaminated coolers, odors, etc. Observations and any exceptions are noted on the Sample Receipt Exceptions Report

4. Sample receipt logging
   a. Verify that the suite of samples and containers received are consistent with the analyses requested on the Chain of Custody. Record all exceptions in the Sample Receipt Exceptions Report.
   b. Assign to each sample a unique laboratory sample identification number (Lab Sample ID). The Lab Sample ID is composed of three parts: the laboratory code, the batch number, and the sample number. This process is programmed into our LIMS system and is done automatically as the samples are inputted.
      i. The laboratory code is used to distinguish between samples originating in the laboratory during a particular year followed by the month (i.e. Samples received in November, 1999 would be assigned the laboratory code 9911).
      ii. The assigned batch number is based on a sequential sample custody number that is maintained by LIMS. A group of samples submitted for analysis at one time comprise a batch unless there are a large number of samples. If this is the case, then with the client's permission, the batches are formed in groups of 20 sample sites. LIMS assigns the next available batch number.
      iii. The sample number within the batch is generally assigned to the samples in the same order as they appear on the Chain of Custody.
      iv. Lab sample IDs will take the form 9911-123-01, 9911-123-02, 9911-123-03, etc.
      v. When multiple containers are received for the same analysis (same preservative and bottle size) on a single sample, or when the sample is to be split, each container will be given an identifying number.
         a) For example, three vials are received for VOA analysis. These containers will all be marked 9911-123-01 and pH will be measured using one of the three vials.
   c. Transcribe the Lab Sample ID to the COC.
   d. Label each sample container with the assigned Lab Sample ID.
5. Verification of sample preservation. Documentation of sample preservation is done using the project specific COC and any exceptions are noted in the Sample Receipt Exceptions Report. Sample preservation is verified as follows.
   a. Temperature verification
      i. Note the presence/absence of ice in the shipping container. If ice is not present in the shipping container, document the exception on the COC.
      ii. Remove the temperature blank and measure its temperature. Record the temperature on the project specific COC.
      iii. If there is no temperature blank in the shipping container, measure the temperature of the ice water in the cooler and record it in the project specific COC.
      iv. If the temperature of the temperature blank or ice water exceeds 4°C (±2°C), an exception has occurred and must be recorded in the Sample Receipt Exceptions Report.
   b. Verification of samples designated for VOA analysis.
      i. Check water samples designated for volatile organic compound analysis (VOA) for adequate preservation as follows. These samples should be in designated 40 mL VOA vials.
         a) Count the number of VOA vials received for each sample.
         b) If there are fewer than three vials, document the exception on the COC.
         c) Select one of the VOA vials for each sample, open and check the pH by immersing a pH strip into the sample. Allow the color to develop. Perform this operation under a hood or other ventilated area.

d) Compare the color on the developed pH strip to the color chart on the pH strip container to determine the sample pH.
   (i) If the pH is less than or equal to 2, record "pH≤2" on the COC.
   (ii) If the pH is greater than 2, record the actual pH measured on the COC. Since this is an exception, document inappropriate sample preservation on the COC and the Sample Receipt Exceptions Form.
e) Mark the vial used to verify the pH by marking a line across the lid of the sample.
f) DO NOT ADJUST VOA SAMPLE pH UNDER ANY CIRCUMSTANCES.
   (i) Inspect all VOA samples for headspace or bubbles. If the headspace is greater than 1% of the vial volume or bubbles are greater than 5 mm (approx. ¼"), make a notation on the COC and the Sample Receipt Exceptions Form.

ii. Store VOA samples in vial boxes after preservation verification in the laboratory.

c. Verification of samples designated for other analyses
   i. Samples designated for certain analyses also require verification of preservation
   ii. Open the sample container inside a hood or other well-ventilated area.
   iii. Pour an aliquot of sample into disposable beaker cups.
   iv. Immerse pH strip into the cup and remove. Allow color to develop.
   v. Compare the color on the developed pH strip to the color chart on the pH strip container to determine the sample pH.
      a) If the pH is within criteria, record the criterion on the COC. For example, the pH requirement for TOC is pH<2, write "pH<2" on the COC. The pH requirement for Total Cyanide is pH>12; write "pH>12" on the COC.
      b) If the pH is outside criteria, record the actual pH measured on the COC. Since this is an exception, document inappropriate sample preservation on the COC and the Sample Receipt Exceptions Form..
   vi. Discard the disposable cup and its contents. DO NOT DISPENSE ALIQUOTS BACK INTO THE SAMPLE CONTAINER. DO NOT RE-USE DISPOSABLE CUPS.
   vii. Close the sample and proceed to the next one.

6. Splitting Samples. If a sample is received in a single container requesting analysis from different analytical groups, this should be documented on the COC. If there is enough volume present, and it is approved by Project Management, the sample may be split. Listed below is the procedure for splitting soil and water samples.
   a. Soil samples received in glass jars requesting non-volatile analysis can be split using clean stainless steel spatulas. Samples requesting volatile analysis cannot be disturbed under any circumstance until the VOA analysis has been completed.
   b. Unpreserved water samples can be split within 24-48 hours after receipt or if the client requests for a later time. The sample must be homogenized and poured into an unpreserved container.
7. PEL Laboratories, Inc. reserves the right to reject samples for any of the following reasons.
   - No custody seal as required by project
   - No COC provided
   - Preservation inappropriate for analysis requested
   - Sample container inappropriate for analysis requested
   - Sample received out of holding time for analysis requested
   - Incomplete sample information provided
   - Discrepancies between COC and sample labels
   - Samples have high levels of polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/PCDF's)
   - Samples have a high level gross alpha or beta radiation

   a. All exceptions must be documented on the COC and the Sample Receipt Exceptions Form.
   b. If there is no COC or if it is improperly filled out,
      i. Contact the Project Management Department for guidance about creating a COC.
      ii. Create a COC as required by the Project Management department in consultation with the client.
      NOTE: Creating a COC in this manner is not documentary proof of legal chain of custody.
      iii. Send a copy of the COC to the client with a full description of the problem and action taken.

c. The client must be notified in a timely manner of all exceptions by telephone, facsimile (fax), or other suitable means. Documentation of such notification must be maintained in the client notification section of the Sample Receipt Exceptions Report (Figure 2).
d. Sample storage. Distribute the samples to the laboratory for analysis as follows.
    VOA samples
        i. Place the samples in the refrigerator designated for VOA samples.
    ii. Segregate samples into separate areas of the cooler as marked on the shelves.
    Extractable organics samples
        ii. Place the samples in the refrigerator designated for Extractable organics samples.
        iii. Segregate samples into separate areas of the walk-in cooler as marked on the shelves.
    Wet Chemistry
        iv. Deliver samples to the walk-in cooler.
        v. Segregate samples into separate areas of the cooler as marked on the shelves.
e. All paperwork associated with a sample batch is placed in a file folder and stored in Sample Custody.

HEALTH AND SAFETY

All samples should be considered to be hazardous until proven otherwise. Therefore, all reasonable precautions to ensure the health and safety of persons receiving samples must be followed.

Shipping containers and individual samples should be opened under a hood or a well-ventilated area, which ensures that the sample coordinator will not inhale toxic fumes.

All sources of combustion should be kept away from samples.

Noxious odors should be handled by placing the samples in a hood and/or evacuating the area.

Gloves, laboratory coats and safety glasses should be worn.

REFERENCES

N/A

Figure 1. Project Specific Chain of Custody

Figure 2. Sample Receipt Confirmation Sheet

PEL Laboratories, Inc. - Standard Operating Procedure

Sample management: internal chain of custody (COC)

APPROVED:

Team Leader / Sample Custody Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. to ensure a permanent record of sample tracking within the laboratory for those samples requiring full chain-of-custody documentation. Samples requiring this information are Level III, AFCEE, Foreign Soils, samples designated for court cases, etc. The primary objective of sample custody is to generate documentation sufficient to trace a sample from its point of origin, through receipt in the laboratory, analysis, reporting and disposal.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

QA/QC REQUIREMENTS

Not applicable

EQUIPMENT/APPARATUS

- Internal Chain of Custody Logbook (Internal COC)

REAGENTS

N/A

PROCEDURE

After samples are first received in the laboratory, the sample coordinator in the Sample Custody area performs an initial check of the samples and signs the chain of custody form, recording the date and time of receipt.

When laboratory sample identifications have been assigned, preservation verified, and all exceptions or discrepancies documented and/or resolved, the samples are distributed to the appropriate secure storage areas and logged into the internal COC (Figure 1). Only authorized laboratory personnel have access to their specified sample storage areas.

a. Volatile samples are stored in the reach in cooler located in the Sample Custody area
b. Non-volatile samples are stored in a walk-in cooler located in the Sample Custody area.

The analysts remove the samples from the appropriate storage area and document the check out date and time in the Internal COC logbook. The sample custodian will relinquish the samples to the analysts as samples are removed from the coolers. While the samples are checked out, they are in constant view of the analysts, or they are stored in a designated area that is locked and secured.

When the analysts return the samples to their proper storage location, the check in date and time is documented in the Internal COC logbook. The sample custodian will accept the samples from the analysts as the samples are put back into the appropriate locations within the cooler.

CALCULATIONS

NA

REVIEW/VALIDATION

NA

DOCUMENTATION

Upon completion of sample analysis, Custody provides copies of the internal chain-of-custody to the Data Package personnel.

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

NA

Figure 1
Internal Chain Of Custody

PEL Laboratories, Inc. - Standard Operating Procedure

QC activities: Corrective Action System

APPROVED:

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. to document problems that may impact data quality, production efficiency or client relations in formal corrective action reports (CARs).

Quality control elements are used to monitor and assess the validity of sampling and analysis activities. Corrective action will be initiated if data are determined to be of questionable validity or if QC elements are not within required limits. For routine problems, the analysts correct the problem and document such activity in the analytical run log or worksheet.

To the extent possible, PEL Laboratories, Inc. will resolve all situations that require corrective action before data quality is affected. These corrective actions do not require documentation in a formal CAR.

Under special circumstances which require client input or notification (insufficient sample, expired holding times), the client will be consulted about additional actions. Clients will be notified of corrective actions as appropriate.

The Sample Receipt Confirmation sheet is a special form of corrective action report in which problems encountered during sample login are documented. These reports are not considered part of the corrective action system described in this SOP because in most cases the laboratory has no control over situations occurring before the samples arrive in the laboratory. Examples of these are samples with improper preservation, arriving after holding time expiration, broken containers, and so on. These are described in SOP00010-C, *Sample management: initial receipt, inventory, preservation verification, labeling and storage.*

If data are reported whose QC elements are not within criteria, the exceptions will be noted in the case narrative and cross-referenced to the unique CAR number.

Corrective action reports are the responsibility of the entire laboratory staff. Any PEL Laboratories, Inc. employee who becomes aware of a problem with any aspect related to reported data is responsible for initiating a CAR. In most cases, this will be primarily the analysts' responsibility, but any reviewer or person in contact with the client that becomes aware of a problem must initiate a formal corrective action report.

CARs are signed and dated by the appropriate production area manager and by the QA Officer.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Area managers are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

QA/QC REQUIREMENTS

Each corrective action report must be uniquely identified.

EQUIPMENT/APPARATUS

N/A

REAGENTS

N/A

PROCEDURE

1. Documentation of corrective actions
   a. Blank corrective action report forms (Figure 1) are available throughout the laboratory.
   b. Upon encountering a situation that requires formal documentation in a corrective action report, the person who first became aware of the situation initiates the corrective action report.
   c. The corrective action report is divided into several sections, each of which must be completed.
      i. Section 1. Description of the problem.
         1) Date: Write the date the Corrective Action Report was initiated, not the date of the incident.
         2) Project: Write the name of the project affected as it appears in LIMS. If this information is not readily available or not known, write the name of the client.
         3) Batch No: Write the laboratory batch number here. If multiple batches are involved, skip this block.
         4) Samples: Write the numbers of the samples affected. It is expected that the samples affected will be those in the batch listed in the previous block. In this case, you need only write the numbers of the samples within the batch (*e.g.*, 1, 3, and 7). If multiple batches are involved, write the full Laboratory Sample ID (*e.g.*, 9911-215-4, 9912-001-1).
         5) Test: Write the method for which the CAR applies (*e.g.*, TKN, EPA351.3) or some other text that unequivocally identifies the test affected.
         6) Condition / Situation. Describe in as much detail as space allows -- including dates, instruments, names of staff -- the condition requiring corrective action. If the condition involves holding times, describe why the holding times were missed, and fill out the holding time grid. Initial and date the description of the problem in the space left after the description of the problem.
      ii. Section 2. Recommended action. Recommended actions are written in this space.
         1) Any person reviewing the CAR can write a recommended action.
         2) The initial routing of the CAR during this stage must include the client services department, who will write any contribution that they may have to the recommended actions.
         3) All persons recommending actions must initial and date, and keep their comments brief and to the point.
         4) Only approved recommended actions can be implemented. The approval of the recommended action must be documented by the area manager.
      iii. Section 3. Client notification. All corrective action reports are routed (see below) to the Project Management department during the initial stages of the corrective action. Project Management is required, without delay, to notify the client about the situation and document it on the CAR. If the notification is made by facsimile (fax) transmission, this is noted on the form. CARs should not be allowed to go unattended at this point.
      iv. Section 4. Action taken. Describe the corrective action taken and the results of the action. All persons documenting actions taken must initial and date after their comments.
         1) If the action taken occurs in a single department, the "ACTION TAKEN - for single response CARs" block is filled out.
         2) If the action taken occurs over several departments, the reverse of the CAR form is used (Figure 2). The area manager, in consultation with client services, checks off all the areas within the lab that need to respond to the CAR. Each area, in turn, describes the action taken and passes it on to the next in the routing list.
      v. Section 5. Closure. This section is signed by the QA Officer if the corrective actions are in order. By signing the CAR, the corrective action is closed and ready for filing in the QA office.
2. Routing of CARs
   a. After a situation has been identified which requires corrective action, certain persons must be made aware of the existence of such a situation. Therefore, all initiated CARs must be routed to
      i. The impacted area's manager for documented approval of recommended actions.
      ii. The Project Management department for client notification.

b. Under exceptional circumstances, which must be documented on the CAR, this routing may be temporarily skipped.
c. Each person that reviews initiated CARs has the obligation to take the appropriate action within the same day in order not to impede the progress of the corrective action.

3. Unique numbering of corrective action reports
   a. Each corrective action must have a unique number. This number is assigned using the Document Control Number log.
   b. The QA Officer or designee will assign CAR numbers to any person requesting it.
      i. The initiator of the CAR will call the QA Officer and request a CAR number. If this is not possible, the person may access the CAR number log (Figure 3) directly which is located on the QA Officer's desk inside the Information Services trailer.
      ii. The person will find the next available space in the CAR section of the Document Control Numbers log and generate the next available number.
      iii. The person will assign that CAR number to the initiator of the CAR by entering in the log the newly created CAR number, the name of the initiator, the date the number was assigned, and a very brief description of the problem.
      iv. The format of the unique CAR number is described SOP00003-QA, *Controlled Documents.*
4. Cross-referencing corrective action reports in data packages
   a. Whenever a situation which requires a corrective action, the unique number of the corrective action report is included with the report.
   b. In most cases, this is done in the case narrative, with a brief statement describing the situation, and how it was resolved. In order to provide full traceability to the situation, the person writing the case narrative will write in parenthesis the number of the corrective action report after the statements in the case narrative. An example is provided in Figure 4.
5. Permanent filing of corrective action reports
   a. Original and closed corrective action reports are permanently filed in the QA files of the laboratory.
   b. Copies of the corrective action reports may be included with project files, but this is not absolutely necessary, because of the cross-references to reports described above.

DOCUMENTATION

Documentation must follow the requirements in SOP00040-QA, *Rules for documentation.*

REFERENCES

- PEL Laboratories, Inc. Quality Manual, Revision 2, 12/3/99

Figure 1. Corrective Action Report Form (side 1)

CAR Unique ID: _____

DESCRIPTION OF PROBLEM – to be filled by the person who first becomes aware of problem

Date:_____ Project:_____

Batch Number:_____ Samples:_____ Test: _____

Condition / Situation (All persons must initial and date): _____

_____

_____

_____

_____

_____

Missed Hold Time Grid (Specify reasons for missed hold times above)

Sample Number	Client Sample ID	Date Collected	Date Prep'd / Anal'd	Days Out of Hold

RECOMMENDED ACTION – to be filled by Originator, Supervisor, and / or Project Management

All persons recommending action must initial and date: _____

_____

_____

_____

CLIENT NOTIFICATION (if applicable) – to be filled by Project Management

Date Notified:_____ Person Contacted:_____

Client's Comments: _____

_____

_____

_____ Signature / Date: _____

ACTION TAKEN – for single response CARs

See reverse side for multiple response CAR routing and actions taken

All persons documenting action must initial and date:_____

_____

_____

_____

_____

CLOSURE – to be filled by QA Officer

All corrective actions have been implemented.

_____

PEL Laboratories, Inc. QA Officer Date

Figure 2. Corrective Action Report Form (side 2)

ROUTING – to be filled by Project Management or QAO
All areas marked are required to describe the action taken

__ Organics – Analytical __Inorganics – Analytical __ Information Services __Data Packaging
__ Organics – Reporting __Inorganics – Reporting __ Project Management __QA Officer

Department:_____
Action Taken:_____
_____
_____
_____
Signature / Date_____

Department:_____
Action Taken:_____
_____
_____
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Signature / Date_____

Department:_____
Action Taken:_____
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Department:_____
Action Taken:_____
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Signature / Date_____

Department:_____
Action Taken:_____
_____
_____
_____
Signature / Date_____

Figure 3. CAR Section of the Document Control Number Log

Figure 4. Case Narrative With CAR reference

PEL Laboratory- Standard Operating Procedure

Sample Preparation: Digestion of Liquid and Solid Samples for Cations Analyses

APPROVED:

Trace Metals Team Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratory to digest water, sediment, soil and other solid samples for analysis by GFAA and ICP.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

QA/QC REQUIREMENTS

The holding time for aqueous and solid samples is 180 days.

This SOP was written to conform with all QA/QC criteria described in the following methods: SW-846 3005A, 3010A, 3020A, 3050B, EPA (200.7).

Samples must be prepared and analyzed as part of an analytical batch. An analytical batch is defined as a set of samples, not to exceed 20 field samples, of the same matrix that: are prepared within the same 24-hour period, using the same techniques and reagents; are associated with a suite of QC samples; and are analyzed together in a continuous manner. For AFCEE work, the matrix spike and matrix spike duplicate are counted as part of the 20 samples in the batch, therefore only 18 field samples can be digested per batch. The analytical batch and the "AFCEE Analytical Batch (AAB)" is defined in the sample preparation step. Table 1 lists the QC requirements that impact sample preparation.

At times it may be necessary to break a batch for analysis. This implies that some of the samples in the batch are analyzed during a different or non-continuous time interval as the others, or on a different instrument. In these cases, the method blank associated with that batch will be analyzed with the separated portions of the batch.

EQUIPMENT/APPARATUS

Electric hot block, adjustable and capable of maintaining a temperature of 90-95°C.
55mL Heat resistant, polypropylene beakers and caps.
Heat resistant, polypropylene Watch glasses

REAGENTS

1. ASTM Type II water
2. Concentrated nitric acid (HNO_3), specific gravity of 1.41 (J.T. Baker Instra-Analyzed. CAT# 9598-34)
3. Concentrated hydrochloric acid (HCl), specific gravity of 1.19 (J.T. Baker Instra-Analyzed. CAT# 9530-33)
4. Hydrogen peroxide (H_2O_2) (30%) (J.T. Baker ULTREX CAT# 5170-01)
5. LCS and matrix spike solutions are listed in Tables 2-4. Spikes are added to the native sample (or appropriate blank material) before beginning the digestion procedure. (CPI Spike #1 CAT#4400-130857, Spike #2 CAT#4400-130856)

PROCEDURE

I. Water sample digestion methods

A. SW846 3005A or EPA 200.7 Acid Digestion of waters for total recoverable or dissolved metals for analysis by ICP spectroscopy.

1) When analyzing for total dissolved metals filter the sample through a 0.45 micron filter, at the time of collection, prior to acidification with nitric acid.
2) For the determination of dissolved elements, the filtered, preserved sample may be analyzed as received. (EPA 200.7) NOTE: (PEL's policy is to digest every sample. The samples are run undigested only per client's request or for analytical confirmation.)
3) Transfer a 50-mL aliquot of well-mixed sample to 50mL polypropylene beaker.
4) Add to the sample the following acids: 1 mL of concentrated HNO_3 and 1mL of conc. HCl [SW846 3005A].
5) Cover the beaker with a watch glass and heat on hot block at 95°C until the sample volume is reduced to ~20 mL. DO NOT BOIL.
6) Remove the beaker and allow to cool. Bring the digestate to a final volume of 50 mL using ASTM Type II water. Cap the beaker and shake it vigorously to thoroughly mix contents.

B. SW-846 3010A Acid digestion of aqueous samples and extracts for total metals for analysis by ICP Spectroscopy.

1) This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids. The procedure is used to determine total metals.
2) Transfer a 50 mL representative aliquot of the well-mixed sample to a 50mL polypropylene beaker and add 3 mL of conc. HNO_3 and 2.5 mL of conc. HCl.
3) Cover the beaker with a watch glass and place on a hot plate and cautiously evaporate to a low volume (10 mL). DO NOT BOIL or allow sample to go dry.
4) Remove the beaker and allow it to cool. Bring the digestate to a final volume of 50 mL with ASTM Type II water. Cap the beaker and shake it vigorously to thoroughly mix contents. The final acid concentration is approximately 6% HNO_3 and 5% HCl.

C. SW 846 3020A Acid digestion of aqueous samples and extracts for total metals for analysis by GFAA spectroscopy.

1) This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids. This procedure is used to determine the total amount of the metal in the sample.
2) Transfer a 50 mL representative aliquot of the well-mixed sample to a 50mL polypropylene beaker and add 1 mL of concentrated HNO_3.
3) Cover the beaker with a watch glass and place the beaker on a hot plate and cautiously evaporate to a low volume (10 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry.
4) Remove the beaker and allow it to cool. Bring the digestate to a final volume of 50 mL with ASTM TYPE IIwater. Cap the beaker and shake it vigorously to thoroughly mix contents.

II. Preparation of Non-aqueous Samples - Soil, Sediment, Sludge, Tissue

A. SW-846 3050B - Acid digestion procedure for ICP analysis of non-aqueous samples

a) Mix the sample thoroughly to achieve homogeneity. Weigh (to the nearest 0.01 g) a 0.50 g portion of the sample and transfer to a 50mL polypropylene beaker.
b) Add 5 mL of ASTM Type II water, 7.5 mL of conc. HNO_3, mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 90 minutes without boiling. Allow the sample to cool.
c) After the sample has cooled, add 2.5 mL of 30% H_2O_2. (NOTE: 3 mL of H_2O_2 may cause a vigorous reaction). Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.
d) After cooling, add 2.5 mL of conc. HCl. Replace the watch glass and place back on the hot block for 30 minutes.

e) Remove the beaker and allow it to cool. Bring the digestate to a final volume of 50 mL with ASTM TYPE IIwater. Cap the beaker and shake it vigorously to thoroughly mix contents.

CALCULATIONS

Not Applicable

DOCUMENTATION

Documentation of digestion is done on a Digestion Log (DIG Sheet), see Figure 1.

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

- Metals, *Methods for Chemical Analysis of Water and Wastes,* U.S. EPA 200.7
- Acid Digestion of Aqueous Samples for Metals - FAA/ICP, *Test Methods for Evaluating Solid Waste (SW-846),* U.S. EPA, Third Edition, SW846- 3005A
- Acid Digestion of Aqueous Samples for Metals, *Test Methods for Evaluating Solid Waste (SW-846),* U.S. EPA, Third Edition, SW846- 3010A
- Acid Digestion of Aqueous Samples - Metals/GFAA, *Test Methods for Evaluating Solid Waste (SW-846),* U.S. EPA, Third Edition, SW846- 3020A
- Acid Digestion of Sediments, Sludges & Soils, *Test Methods for Evaluating Solid Waste (SW-846),* U.S. EPA, Third Edition, SW846- 3050B

Table 1. QC requirements for analytical batches for cations sample preparation.

	EPA 200.7	AFCEE	SW846
Valid matrix	Water	Water and Solids	Water and Soils
Analytical batch size[a]	20 field samples	18 field samples	20 field samples
Method blank	one per batch	one per batch	one per batch
Matrix spike	one per matrix per batch	one per matrix per batch	one per matrix per batch
Matrix spike duplicate	one per matrix per batch	one per matrix per batch	one per matrix per batch
Laboratory control sample	one per matrix per batch	one per matrix per batch	one per matrix per batch

[a] The analytical batch size does not include any QC samples listed here and is not intended to. For example, if the analytical batch size is 20, the total number of samples in the batch will be 24 (20 field samples, one blank, one matrix spike, and duplicate or MSD, and one LCS). Except for AFCEE work which does count the matrix spike and matrix spike duplicate as samples.

Table 2. LCS and Matrix Spike Solutions (ICP)

Element	Solution Conc. (ppm) (µg/mL)	Effective Sample Conc. (ppb) (µg/L)
Ag	25.0	500
Al	2500	50000
As	25.0	500
Ba	25.0	500
Be	25.0	500
Ca	2500	50000
Cd	25.0	500
Co	25.0	500
Cr	25.0	500
Cu	25.0	500
Fe	2500	50000
K	2500	50000
Mg	2500	50000
Mn	25.0	500
Mo	25.0	500
Na	2500	50000
Ni	25.0	500
Pb	25.0	500
Sb	25.0	500
Se	25.0	500
Sn	25.0	500
Tl	25.0	500
V	25.0	500
Zn	25.0	500

Add 1.0 mL of Spiking Solution #1and #2 to 50 mL of an aqueous sample or 0.50 g of a solid sample when the final volume is 50 mL.

Table 3. TCLP Spiking Solution (ICP)

Element	Solution Conc. (µg/mL)	Effective Sample Conc. (µg/L)
Ag	25.0	500
Ba	25.0	500
Cd	25.0	500
Cr	25.0	500
Pb	25.0	500
As	25.0	500
Se	25.0	500

Add 1.0 mL of the TCLP Spiking Solution to 5.0 mL of the TCLP extract (final volume = 50 mL).

Table 4. LCS and Matrix Spike Solution (GFAA)

Element	Solution Conc. (µg/mL)	Effective Sample Conc. (µg/L)
As	25.0	50.0
Tl	25.0	50.0

Add 100 µL of Spiking Solution #1and Spiking Solution #2 to 50 mL of an aqueous sample

Digestion For: ICP By Whom: _____

Spikes: 1.0 ml/sample
Multi-element # Date: _____
#

Beaker #	Sample	ID #	Wt (g)	spiked	Beaker #	Sample	ID #	Vol (ml)	spiked	YN Comment or Notification
	SB-DigBlk	PBS	50ml			WB-DigBlk	PBW	50		* * HCl lot#
	SS-DigSpk	LCSS	50ml			WS-DigSpk	LCSW	50		* * HNO3 lot#
										* * H2O2 lot#
		ms					ms			
		msd					msd			

Figure 1 Digestion Log

PEL Laboratories inc. - Standard Operating Procedure

Sample Preparation: SW846 Herbicide Extraction for Method 8151/EPA 615

APPROVED:

Sample Prep Team or Section Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories to isolate certain chlorinated acid herbicides from soil/sediments and aqueous samples; which may be present in the original sample in the form of an acid, salt, or a neutral derivative of the herbicide such as an ester. Extraction methods SW-846 for 3550B (See SOP00025-P) and 3510C (See SOP00022-P) offers extraction procedures based on the concentration of herbicides in the sample. Method 615/8151 may be used to determine the following compounds:

Compound	CAS No.[a]
2,4-D	94-75-7
2,4-DB	94-82-6
2,4,5-TP (Silvex)	93-72-1
2,4,5-T	93-76-5
Dalapon	75-99-0
Dicamba	1918-00-9
Dichloroprop	120-36-5
Dinoseb	88-85-7
MCPA	94-74-6
MCPP	93-65-2
4-Nitrophenol	100-02-1
Pentachlorophenol	87-86-5

[a] Chemical Abstract Service Registry Number

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the technician, and providing adequate explanation of the material contained.

QA/QC REQUIREMENTS

The holding time is 7 days for aqueous and 14 days for soil/sediment samples.

This SOP was written to conform to all QA/QC criteria described in the following methods: EPA methods SW846-3550B & 3510C for Method 8151/EPA 615.

INTERFERENCES

1. Phthalate esters that are easily leached from plastics can interfere when using the electron capture detector. Avoiding contact with any plastic materials during extraction can minimize interference.
2. Contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms may cause Method interference.
3. The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

EQUIPMENT/ APPARATUS

1. Boiling chips: Muffled carborundum
2. Steam Bath: Heated, with concentric ring cover
3. 2mL amber crimp top vials
4. Graduated cylinder: 250mL Class A
5. Macro-Snyder column: 3-ball
5. Micro-Snyder column: 2-ball
6. K-D concentration tube: 10mL
7. K-D flask: 500mL
8. 4mL disposable glass pipettes
9. Long tip Pasteur pipettes: disposable, borosilicate glass
10. Volumetric Hamilton syringes (Class A), assorted sizes
11. 250mL Erlenmeyer flask
12. Glass Wool
13. Clear 40mL VOA vials
14. Aldrich Diazald, Ming Diazomethane Generator kit
15. Separatory funnel: 2L
16. 500mL Erlenmeyer flask
17. 1L Erlenmeyer flask
18. Glass funnels
19. Whatman #41 filter paper
20. Vented Stoppers

REAGENTS

1. Preparation of Acidified Sodium Sulfate-Sodium sulfate (granular, acidified, anhydrous), Na_2SO_4 - Purify by heating at 160^0 C for 12 hours (muffle furnace), in a shallow tray. Acidify by slurring 1000-g sodium sulfate with enough diethyl ether to just cover the solid; then add 10mL of concentrated sulfuric acid and mix thoroughly. Remove the ether by heating in steam bath on medium. Store at 104-deg C (Muffle Furnace)
2. Solvents
   a) Extraction Solvent – Methylene Chloride (DCM), pesticide quality or equivalent.
   b) Extraction Solvent - Acetone, pesticide quality or equivalent.
   c) Exchange Solvent - Methyl tert-Butyl Ether (MTBE), ACS grade.
   d) Extraction Solvent - Ether ACS grade.
2. Sulfuric acid (1:1), ACS grade.
3. Methanol (MeOH), ACS grade.
4. Diazomethane: See Diazald Kit and manufacturer's instructions for preparation.
5. Florisil F100-500 60-100 Mesh (Fisher Scientific).
6. Stock Standards-Primary stock standard for calibration and spiking is the "underivatized" chlorinated acid herbcide solution, M8150A, from AccuStandard. The secondary stock standard is the "underivatized" chlorinated acid herbicide solution, EMP80410, from EM Science Co. Both of the above solutions consist of the following components at the listed concentrations in methanol.

Component	Concentration (ug/mL)

Dalapon	100
Dicamba	100
MCPP	10000
MCPA	10000
Dichloroprop	100
2,4-D	100
2,4,5-TP (Silvex)	100
2,4,5-T	100
2,4-DB	100
Dinoseb	100

Calibration Standards

Use the primary standard for preparation of the calibration standards for derivatization. This is done at the same time as the samples are derivatized. The secondary standard is used to prepare only one standard to be derivatized at the level of the midpoint of the calibration curve. The secondary standard will be used to confirm the accuracy of the primary standard. Before spiking, prepare a 1:10 dilution using class A volumetric glassware and syringes of the above stock solutions in acetone to obtain a working spike at 10ug/mL (MCPP + MCPA at 1000 ug/mL).

When it is necessary to analyze for Bentazon, a stock solution, F20385, from Chem Service at 100ug/mL in acetone is used. The working solution is a 4:10 dilution in acetone at 40ug/mL.

When it is necessary to analyze for Picloram, a stock solution, F2041S, from Chem Service at 100ug/mL in acetone is used. Prepare a working solution at 10ug/mL in acetone.

Surrogate Stock Standards-The primary stock for surrogate is Ultra, PP5-160, 2,4-dichlorophenylacetic acid solution in MTBE at 100ug/mL. The working level is at 10ug/mL in MTBE. Use primary working level for all calibration standards, QC spikes and samples.

Primary internal standard is Ultra Scientific PPS-170, 4,4-dibromooctaflourbiphenyl (DBOB), in MTBE solution at 100ug/mL. The working level of the internal standard is 10ug/mL in MTBE. Use primary working level for all calibration standards, blanks and samples.

PROCEDURE

1. Extraction for Soils

a. Using a Hamilton syringe, add 250uL of herbicide surrogate solution to all the samples.
b. For MS/MSDs and LCS, also add 100uL of herbicide acid spike solution.
c. Samples are extracted using the sonication method 3550B (See SOP00025-P).
d. After extraction, extracts are allowed to sit for two hours in the 500mL Erlenmeyer flask with enough acidified sodium sulfate added to cover the bottom of the flask before concentrating. Add the extract and boiling chips and a macro-Snyder column to the K-D flask.
e. Concentrate to approximately 1mL.Sample extracts are exchanged into MTBE by adding approximately 5mL with a pipette through the macrosynder and concentrated again to approximately 4mL.

1.a. Extraction for Liquids

a. Measure approximately 1,000mL of sample and place in a 2liter separatory funnel.
Exceptions: 1. If there are two or more obvious layers, notify your supervisor. In this situation, the client

must be notified to determine the layer of interest.

2. *If the sample is unusually dirty or has a very strong odor, notify your supervisor. In this situation, it may be necessary to cut back on the initial volume to be extracted.*

b. Adjust the pH to <2, using concentrated (1:1) sulfuric acid.
c. Add 250uL of herbicide surrogate solution to the sample using a volumetric syringe.
d. For MS/MSDs, also add 100uL of herbicide acid spike solution.
e. Add 150mL of Ether using a 250mL-graduated cylinder to the sample.
f. Shake for 4 minutes using an orbital shaker table using vented stoppers.
g. Allow phase separation to occur (~5 minutes). When separation is complete, drain the aqueous portion (bottom) into a 1000mL Erlenmeyer flask. Then, drain the Ether (top) layer into a 500mL Erlenmeyer flask with a glass funnel containing Whatman #41 filter paper and muffled, granular acidified Na_2SO_4.
h. Add the aqueous portion back to the separatory funnel.
i. Add 50mL of ether to the aqueous layer and repeat steps f through h two additional times.
Note: If emulsions form, collect the ether from the separatory funnel into a 250mL beaker. Add sodium sulfate to the extract in the beaker and swirl until the emulsion is broken up. Add the extract back to the 500mL Erlenmeyer flask.
j. After extraction, extracts are allowed to sit for at least two hours in the 500mL Erlenmeyer flask with enough acidified sodium sulfate to cover the bottom of the flask. Add the extract and boiling chips and a macro-Snyder column to the K-D flask.
k. Set water bath temperature at 15-20-deg C above the boiling point of the solvent. The boiling point of Ether is 34.55-deg C. Therefore, the water bath temperature is to be maintained between 49.55-deg C and 54.55-deg C.
l. Concentrate to approximately 4mL. Sample extracts are exchanged into MTBE by adding approximately 5mL with a pipette through the macrosynder and concentrated again to approximately 4mL.

8151 TCLP

The extraction method is 3510C and prepared by method 1311 (TCLP). A sample spike must accompany one TCLP sample out of the batch. The maximum volume used is 500mL.

a. Take approximately 1L of the TCLP sample and split into two equal portions using a 1000-mL graduated cylinder and transfer to a separatory funnel.
b. Add 250-uL of Herbicide surrogate solution to the samples
c. Add 100-uL of Herbicide spike acid solution to one sample and label it accordingly.

Repeat steps e thorough l from the extraction section.

2. Preparation of Calibration standards

Prepare a blank plus eight different concentrations for each parameter of interest, through dilution of the stock standards with Methyl tert-Butyl Ether. Dilute to 5mL using MTBE in a volumetric flask. One of the standards should be at a concentration near, but above, the method detection limit. The remaining standards should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months or sooner if comparison with check standards indicates a problem. Use the primary working level for all calibration standards and blanks. (Note that the calibration standards can be repreped in order to use in future analysis as long as the Diazomethane used for derivatzation of the future samples is from the same lot.)

Calibration Standard (g/L)	Blank	25	50	100	150	200	250	300	$150_{(secondary)}$
Actual Conc. (ug/mL)	0	0.025	0.050	0.100	0.150	0.200	0.250	0.300	0.150

Primary working spike (uL)	0	25	50	100	150	200	250	300	150
Primary working surrogate (uL)	0	25	50	100	150	200	250	300	150
Second source working Spike (uL)	0	0	0	0	0	0	0	0	150

3. Derivatization

Calibration standards are prepared at this time and derivitized along with the samples to be analyzed. After all calibration standards are prepared and all the samples have been reduced and solvent exchanged to MTBE, diazomethane is added to the samples. Diazomethane is added until the sample turns yellow in color. This color must be maintained for at least thirty minutes. More Diazomethane may be added if required. If more than 5mL of Diazomethene are required, a 1:10 dilution is made of the sample and the Diazomethane addition is repeated. Dilutions are recorded in the extraction logbook. After the color is maintained in the sample extracts for thirty minutes, the excess Diazomethane is driven off by heat. Add a new boiling chip to the KD tubes and heat the sample on the steam table until no yellow color is observed. At this time, proceed to the Florisil cleanup.

4. Florisil Cleanup

All samples and standards must be cleaned with Florisil. Use 0.5g of Florisil and pack in a 4mL-glass pipette. Add the entire sample to the column and elute with a 5% MeOH/MTBE solution. DO NOT ALLOW the column to become dry. Collect the elutent in a 10mL volumetric flask. Continue to add the 5% MeOH/MTBE solution until the collected volume is 10mL. This is done for every sample.

5. Vialing

a. The Florisil cleaned samples are placed in marked 40mL VOA vials; labeled with test name, project number, sample number and extraction date.
b. An amber crimp vial is prepared with the test number, sample number, and date, and wis (with internal standard).
c. A 500uL portion of the stock sample in the VOA vial is put into the 2ml amber vial using a 500uL Hamilton syringe. Added to this is 5uL of internal standard.
d. Follow procedure with all samples and quality control.
e. Put stock 40mL vials into archive boxes noting box and row numbers in the appropriate spaces of the logbook, store in refrigerator C in sample preparation lab. Make copies of logbook, and put working extractions into analyst sample refrigerator in Semi-Vols.

CALCULATIONS

You will need to be familiar with calculating spike, surrogate, and reagent concentrations. Please have your section supervisor peer check your calculation prior to making any solutions. Never assume the last analyst made the solution correctly. Double check their calculations as well.

REVIEW/VALIDATION

Review of extraction logbook before release is the responsibility of the Sample Prep. Team Leader or designee. The logbook will be reviewed for completeness and signed before copies are made for the appropriate analytical area.

DOCUMENTATION

The technician performing the work will make the appropriate documentation. The technician is responsible for finding a peer to witness the addition of spike to the QC samples. The spike witness must sign off on the extraction log in the appropriate location.

Any difficulties encountered during sample preparation will be noted on the extraction log. Examples of events that should be documented are emulsions, loss of sample or extract, odor, difficulty-concentrating extract, and samples and received in incorrect containers (this should primarily be documented by sample custody). Such notes are useful if and when corrective action is necessary.

Per laboratory policy, any changes to information in the extraction logbook should be made by drawing a single-line through incorrect information writing the correct information. The person making the change will then initial and date the change. *Rules for Documentation: SOP00040-QA*.

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are highly recommended by management. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager. Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

Ether: Air/Ether mixtures greater than 1.85% volume are considered explosive. Ether may explode if brought in contact with anhydrous Nitric acid. Therefore, ether is not mixed with any reagents other than those outlined in the 8151 SOP method. Inhalation of ether can be narcotic; therefore, ether levels are monitored to prevent excessive exposure. Please see your supervisor or Safety Officer with any questions or concerns regarding Ether usage.The State of Florida regulates ether possession and sale. At no time is Ether to be distributed by PEL Laboratories or its employees to any other person or company.

While Ether is in use in the laboratory prep building it is required to post the magnetic signs labeled "Ether in use" on the entrance to notify all laboratory personnel and visitors of its presence in the building.

POLLUTION AND PREVENTION

Pollution and Prevention encompasses any technique that reduces or eliminates the quantity and/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

For more information about pollution prevention consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477

WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable Federal, state, and local rules and regulations. 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 sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further informa-

tion on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477

REFERENCES

- Test Methods for Evaluating Solid Waste: Physical/Chemical Methods SW-846 (3rd Edition) Method 8151
- Determination of Chlorinated Herbicides in Municipal and Industrial Wastewaters, Method 615
- Test Methods for *Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 3550B
- Test Methods for *Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 3510C
- SOP00040-QA *Rules for Documentation*
- SOP00084-P, General Extraction SOP

PEL Laboratories, Inc.- Standard Operating Procedure

Sample Preparation: SW-846 3510C Separatory Funnel Extraction

APPROVED:

Sample Prep. Team Leader Date

Sample Prep. Section Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories to isolate organic compounds from aqueous samples by separatory funnel (liquid-liquid) extraction for subsequent analysis using the following method: SW-846 3510C. Specific extraction conditions can be found in Table 1 for the following methods: 608/8081/8082, 614/8141, 625/8270, 610/8310, FL PRO and 8015 DRO.

This method is applicable to the isolation and concentration of water-insoluble and slightly water soluble organics in preparation for a variety of chromatographic procedures.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the laboratory technician, and providing adequate explanation of the material contained. This SOP is restricted to use by or under the supervision of trained technicians. Each technician must demonstrate the ability to generate acceptable results with this SOP.

The following methods require special instructions or more in-depth descriptions:

Refer to SOP00023-P and SOP00024-P for TX1005 extraction techniques.

Refer to SOP00087-P for 8011 extraction techniques.

Refer to SOP00088-P for 615/8151 extraction techniques.

Refer to SOP00076-P for 8330 extraction techniques.

Please refer to the following PEL SOPs for guidance prior to extracting:

Refer to the standards table SOP00089-P for spike, standard and surrogate preparation.

Refer to SOP00084-P for general extraction/QA procedures.

PRINCIPLE OF OPERATION

A solute may be soluble in many solvents, which are immiscible. When a solution of that solute in one of two immiscible solvents is shaken vigorously with the other immiscible solvent, the solute will be distributed between the two solvents in such a manner that the ratio of the concentrations of the solute is constant. This ratio is called the distribution coefficient, and it is independent of the volumes of the two solvents and the total concentration of the solute.

This type of extraction transfers a solute from one solvent to another. It can be used to separate desired substances from others in solution. The separatory funnel is used for this purpose. Immiscible solvents, which are incapable of mixing with each other to attain homogeneity and will separate from each other into separate phases, must be used. Multiple extractions with smaller portions of the extraction solvent are more effective than one extraction with a large volume. The choice of extraction solvent determines whether the solute remains in the separatory funnel or in the solvent, which is drawn off. The solvent, which has the greater density, will be the bottom layer. Thus the less dense extraction solvent remains in the separatory funnel, and the more dense extraction solvent is drawn off.

Typically the separatory funnel should be large enough to hold twice the total volume of the solution and the extraction solvent.

QA/QC REQUIREMENTS

This SOP was written to conform to QA/QC criteria described in the following methods: SW-846, 3510C

Contaminants in solvents, reagents, glassware, and other sample processing may cause method interferences. Method blanks are prepared with the field samples to demonstrate that the laboratory process is free of such contaminants. A method blank is laboratory reagent water that is taken through the same procedure as all other samples.

Glassware must be scrupulously cleaned. (See SOP00072-P)

Surrogates are added to all samples (including QC samples) immediately before extraction to monitor the success of each sample preparation. Poor surrogate recovery requires investigation. Re-extraction is the logical corrective action if sufficient raw sample is available and if the holding time has not expired. Where no method or program limits are mandated, acceptance limits will be determined using laboratory data.

Matrix spikes and matrix spike duplicates (MS/MSD) are prepared by spiking an aliquot of an environmental sample with known quantities of the method analytes. If no spiking requirements are communicated, spiking will be performed as specified in applicable method. The MS/MSD is analyzed exactly like a sample, and its purpose is to determine whether sample matrix contributes bias to the analytical results by determining the accuracy of each and the precision associated with the spikes. The background concentrations of the analytes in the native sample must be determined in a separate aliquot and the measured values in the MS/MSD corrected for native concentration. If the client has not identified samples to be spiked, laboratory blank water will be used for spiking. The laboratory will prepare MS/MSD at a frequency of 1 set per 20 samples. **For AFCEE**, the MS/MSD count as samples in the batch of 20. MS/MSD results will be compared to established laboratory limits for acceptability. Since the native matrix may have a detrimental effect on accuracy and precision, a LCS is prepared with every MS/MSD. If MS/MSD does not meet acceptance criteria and the associated LCS is acceptable, matrix effect is assumed. Where no method or program limits are mandated, generic limits will be used until in-house limits are determined using laboratory data.

A laboratory control sample (LCS) is prepared by spiking representative target compounds into a blank matrix (laboratory blank water). The LCS is processed through the same extraction, concentration, and cleanup procedures as the samples. Where no method or program limits are mandated, generic limits will be used until in-house limits are determined using laboratory data.

EQUIPMENT/APPARATUS

1. 2 L Separatory Funnel

2. Vented Snorkel Stoppers
3. Retainer Straps
4. 3-D Shaker Table
5. 250mL, 500mL Erlenmeyer Flask
6. Turbovap™ tubes
7. Zymark Turbovap™: N_2 blowdown unit
8. Glass funnels
9. Whatman #41 filter paper
10. 1000mL graduated cylinder
11. 60mL repeating pipettor w/2L Flask
12. Steam table: Heated with concentric ring cover.
13. pH paper 0-14 range.
14. Hamilton (Class A) volumetric syringes, assorted sizes.
15. Glass wool, hexane rinsed.
16. 500mL KD Receiving flasks
17. 10mL Concentrator tubes
18. 3-ball Macro-Snyder column
19. 2-ball Micro-Snyder column
20. 2mL amber vials with crimp tops
21. 40mL clear VOA vials
22. Pipettes: disposable, borosilicate glass
23. 10mL volumetric flasks
24. Acrodisc 13mm, Gelman Scientific

REAGENTS

1. Organic-Free Reagent Water.
2. Methylene Chloride (DCM), pesticide grade or equivalent.
3. Concentrated Sulfuric acid (1:1).
4. Concentrated Hydrochloric acid (1:1).
5. Concentrated Sodium Hydroxide 50% (w/w).
6. Sodium Sulfate (Na_2SO_4): Granular, anhydrous, muffled at 200°C for ~8 hours, cooled, and stored in glass jars.
7. Hexane, pesticide grade or equivalent.
8. Acetonitrile(ACN), pesticide grade or equivalent.

PROCEDURE

1. Prepare (rinse) all glassware with the extraction solvent, generally DCM.
2. Take pH of sample and record. If pH is not in target range (Table 1) adjust with either (1:1) H_2SO_4 or 10 N NaOH, as necessary. Note the original pH in the extraction log book if it is not in the target range. Follow same procedure with quality control samples. These samples contain 1 liter of reagent water (DI H_2O).
3. Characterize samples – identify and record the following characteristics:
   a) Color
   b) Odor
   c) Sediment
   d) Volume
   e) Sample Date

4. Volume determination is method and project specific.
   a) Mark the sample bottle at the meniscus with a sharpie™, pour samples into prepared 2-liter separatory funnels. This mark will later be used to determine the amount of sample used (after extraction process is

completed). Refilling the marked sample bottle with water to the line, and then measuring it in a 1-liter graduated cylinder do this. This volume is noted in the proper section in the extraction logbook.

b) Measure 1-L of sample using a graduated cylinder, transfer 1liter of sample to a 2-liter separatory funnel. Record volume in extraction log book.

5. Exceptions for volume extracted
   a) If there are two or more obvious layers, notify the Extraction Team or Section Leader. In this situation, the client must be notified to determine the layer of interest.
   b) If the sample is unusually dirty or has a very strong odor, notify the Extraction Team or Section Leader. In this situation, it may be necessary to reduce the volume of raw sample extracted.
   c) Volume extracted may also be reduced based on historical information.
      i. Samples with severe emulsions frequently have little or no surrogate/spike recovery and therefore volumes are reduced.
      ii. Samples with historically high levels of target analytes may have volumes reduced to prevent contamination of laboratory equiment.

EXTRACTION

1. Add all surrogates and spike to quality control and sample(s) as required by analysis method.
2. Add 60 mL s of methylene chloride to all quality control and samples.
3. Determine Shaking Method per project:
   a) Hand Shaking:
      i) Stopper the top, invert the funnel and vent.
      ii) Vigorously shake the funnel for 2 minutes. Pressure will build up in the funnel rapidly, so vent frequently into a fume hood.
   b) Orbital Shaker Table:
      i) Place the funnel on the orbital shaker table, cap with vented snorkel stopper and secure with retainer straps.
      iii) Vigorously shake the funnel for 4 minutes.
4. Samples are then uncapped and left to settle out for a minimum of five minutes to ensure complete solvent/sample separation.
5. Filter solvent into proper sample receiving vessel, passing the solvent through a pre-rinsed funnel containing sodium sulfate.
6. Repeat steps 2 through 5 two more times.
7. Refer to the Specific Extraction Conditions for Various Determinative Methods (Table 1) for additional details. Extract the sample three times at each pH listed in the table.

Cautions and Techniques

1. Separatory funnels are very fragile and expensive.
2. Make sure the screw cap is completely closed before running the shaker table.
3. The Vented Snorkel stoppers will vent enormously on the first shake so make sure the doors to the cabinet are closed before turning the shaker table on.
4. Traces of insoluble material often collect at the interfaces between the two insoluble liquids. It is extremely difficult to separate the layers without taking some of this material along, but it can easily be removed during drying step.
5. Frequently, when aqueous solutions are extracted with organic solvents, emulsions form instead of two separate and distinct phases. Emulsions are colloidal suspensions of the organic solvent in the aqueous solvent or suspensions of the aqueous solvent in the organic solvent as minute droplets. This situation occurs when the solute may act as a detergent or soap or when viscous and gummy solutes are present. The emulsions is be broken up by draining the extract/emulsion into a beaker, adding sodium sulfate, and swirling it or using a Teflon stirrer and mixing until the solvent is free flowing. Then pour it into the extraction vessel rinsing with the extraction solvent.

Addendums

Method 8015-Dro Concentration

EQUIPMENT/APPARATUS

1. 500mL KD Receiving flasks
2. 10mL Concentrator tubes
3. 3-ball Macro-Snyder column
4. 2-ball Micro-Snyder column
5. Boiling chips solvent rinsed with methylene chloride
6. Steam table (heated), with concentric ring cover
7. 2mL amber crimp top vials
8. Pasteur pipettes, disposable, borosilicate glass
9. Hamilton (Class A) 1.0mL volumetric syringe
10. 250mL Erlenmeyer flask

REAGENTS

1. Surrogate stock solution: o-terphenyl(OTP), NSI 1341 @ 2000ug/mL. See standards table for preparation of working surrogate solution.
2. Raw Diesel fuel 100% pure. See standards table for preparation of working spike solution.

Evaporation

1. Add a boiling chip to the K-D and attach a three ball macro-snyder column to the top. Place the K-D apparatus on the steam table (15-20-deg C above the boiling point of the solvent) and cook down until the extract volume is less than 4mLs. Remove from the steam table and allow to cool at least 10 minutes.
2. Prepare the sample for micro-cook down by attaching a two-ball micro-snyder to the concentrator tube. Place the sample back on the steam table and cook down to a volume of less than 1mL. Allow the sample to cool for at least 10 minutes. Proceed to vialing.
3. Draw out exactly 1mL of sample from the concentrator tube (DCM can be used to bring to volume if needed) utilizing a 1mL Hamilton syringe. Place the extract in a 2mL amber stock vial labeled with test, project number and date. From the stock vial, draw out 500uL and place in another labeled 2mL amber vial to go to Semi-Vols for analysis.

Method 8081/EPA 608 concentration

EQUIPMENT/APPARATUS

1. Turbovap™ tubes

2. Pipettes: disposable, borosilicate glass
3. 10mL volumetric flasks
4. Hamilton Class A Volumetric syringes
5. 40mL VOA vials
6. 2mL amber vials with crimp tops
7. Zymark Turbovap™

REAGENTS

1. Exchange Solvent - Hexane, pesticide quality or equivalent
2. Surrogate stock solution - Ultra Scientific Cat. #ISM-320@200(g/mL. See standards table for preparation of Working Surrogate solution.
3. Spike stock solution – Ultra Scientific OrganoChloride Pesticides Mixture Cat. #US-127@2000(g/mL. See standards table for preparation of Working Spike solution.
4. Internal Standard stock solution – Ultra Scientific Pentachloronitrobenzene

Evaporation and Solvent Exchange

1. Place the Turbovap™ tubes into the Turbovap™ unit (water bath at 50°C) and evaporate the solvent to approximately 1mL using a gentle stream of nitrogen.
2. Add approximately 10mL of Hexane into the Turbovap™ tube and concentrate to approximately 1mL final volume.
3. Quantitatively transfer the extract to a 10mL volumetric flask using a pipette and fill to volume with Hexane.
4. Transfer the well-mixed sample from the 10mL volumetric flask to a 40mL VOA vial by pouring. Each VOA vial is noted with the test number, sample number and the extraction date.
5. A 2mL amber vial is prepared with the test number, sample number and the extraction date.
6. Using a Hamilton™ syringe, transfer 500µL of the extract into the appropriate 2mL amber vial followed by the addition of 5uL of internal standard.
7. The 40mL VOA vials are placed into archive boxes noting box and row numbers in the appropriate spaces of the extraction logbooks and stored at 4°C (±2°C) in the Sample Prep refrigerator C.
8. Take the extracts to Semi-Vols for analysis.

TCLP 1311/8081/608

1.TCLP extraction is prepared by Method 1311.

2. One TCLP must be accompanied by a sample spike. 1L of TCLP extract is split into two equal 500mL portions. One 500mL portion for the sample, and the other 500mL portion for the sample spike. If less volume is available, divide the total volume equally.

3. 8081 TCLP spike consists of the regular pesticide spike.

4. When there are only TCLP samples are present per analytical batch, the extractionist needs only to do a blank, LCS (with normal spike), sample, and sample TCLP spike. No MS/MSD is required.

Method 8082-PCB Concentration

EQUIPMENT/APPARATUS

4. Turbovap™ tubes
5. Pipettes: disposable, borosilicate glass

6. 10mL volumetric flasks
4. Hamilton Class A Volumetric syringes
5. 40mL VOA vials
6. 2mL amber vials with crimp tops
8. Zymark Turbovap™

REAGENTS

1. Exchange Solvent: Hexane, pesticide quality or equivalent.
2. Surrogate stock solution: Ultra Scientific pesticide surrogate standard spiking solution Cat. # ISM-320 @ 200-ug/mL. See working standards table for preparation of working surrogate solution.
3. Spiking stock solution: Ultra Scientific Aroclor 1016 solution Cat. # pp-282 @ 100-ug/mL and Ultra Scientific Aroclor 1260 solution Cat. # pp-361 @ 100ug/mL. See working standards table for preparation of working spiking solution.

EVAPORATION AND SOLVENT EXCHANGE

1. Place the Turbovap™ tubes into the Turbovap™ unit (water bath at 50°C) and evaporate the solvent to approximately 1mL using a gentle stream of nitrogen.
2. Add approximately 10mL of Hexane into the Turbovap™ tube and concentrate to approximately 1mL final volume.
3. Quantitatively transfer the extract to a 10mL volumetric flask using a pipette and bring to volume using hexane.
4. Transfer the well-mixed sample from the 10mL volumetric flask to a 40mL VOA vial by pouring. Each VOA vial is noted with the test number, sample number and the extraction date.
5. A 2mL amber vial is prepared with the test number, sample number and the extraction date.
6. Using a Hamilton™ syringe, transfer 500µl of the extract into the appropriate 2mL amber vial.
7. The 40mL VOA vials are placed into archive boxes noting box and row numbers in the appropriate spaces of the extraction logbooks and stored at 4°C (±2°C) in the Sample Prep refrigerator C.
8. Take the extracts to Semi-Vols for analysis.

Method Fl Pro Concentration

EQUIPMENT/APPARATUS

2. 500mL KD Receiving flasks
2. 10mL Concentrator tubes
3. 3-ball Macro-Snyder column
4. 2-ball Micro-Snyder column

5. Boiling chips solvent rinsed with methylene chloride
6. Steam table (heated), with concentric ring cover
7. 2mL amber crimp top vials
11. Pasteur pipettes, disposable, borosilicate glass
12. Hamilton (Class A) 1.0mL volumetric syringe
13. 250mL Erlenmeyer flask
14. 40mL clear VOA vials

REAGENTS

1. Surrogate solutions:
   a. o-terphenyl (OTP), NSI 1341 @ 2000 µg/mL
   b. Nonatriacontane (C-39), NSI 1339 @ 6000 µg/mL
2. Spike solution: NSI C-443 @ 2000 ug/ml encompassing Petroleum Hydrocarbon componentsC8-C40
3. Silica gel-chromatographic (100-200 mesh)

Concentration

1. Place a three-ball macro Snyder column on the K-D receiving flask.
2. Place the K-D flask on the heated water bath 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. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.
3. When the apparent volume of the liquid appears to be less than 4mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.
4. Remove the K-D receiving flask, place a micro Snyder column onto the concentrator tube, and concentrate to an apparent volume of less than 2mL by cooking it down on the water bath. Let cool again.

SILICA GEL CLEAN-UP & VIALING (MANDATORY)

1. Draw out exactly 2mL of sample from concentrator tube using a volumetric syringe (DCM can be used to bring to volume if needed) and place in a previously prepared VOA vial containing 0.3 g of silica gel. Shake the mixture gently for 30 seconds and allow to settle out. (The purpose of the silica gel is to pull out any oils that may cause interferences with the analysis).
2. Draw out the extract from each VOA vial using disposable glass pipettes and place into a 2mL amber crimp top vial labeled with the test, project and sample number, plus the date. Using another disposable glass pipette, draw out at least 500µl of the sample and place it into a duplicate amber crimp top vial.
3. The first set of vials are placed into archive boxes noting box and row numbers in the appropriate spaces of the extraction logbooks and stored at 4-deg C (+/-2-deg C) in the sample prep. refrigerator C.
4. The second set of vials is taken to Semi-Vols for analysis.

Method 8141/EPA 614 Concentration

EQUIPMENT/APPARATUS

1. Turbovap™ tubes
2. Pipettes: disposable, borosilicate glass
3. 10mL volumetric flasks
4. Hamilton™ Gastight® syringes

5. 40mL VOA vials
6. 2mL amber vials with crimp tops
7. Zymark Turbovap™

REAGENTS

1. Exchange Solvent: Hexane, pesticide quality or equivalent
2. Surrogate solution- Ultra Scientific Cat. # M-1428 @ 500ug/mL. See working standards table for preparation.
3. Spiking solution- Ultra Scientific Cat. 3 SPM-614 @ 200ug/mL. No preparation is necessary for spiking solution, the spike is ready to use.
4. Internal standard- Ultra Scientific PPS-350 @ 1000ug/mL.

Evaporation and Solvent Exchange

1. Place the Turbovap™ tubes into the Turbovap™ unit (water bath at 50°C) and evaporate the solvent to approximately 1mL using a gentle stream of nitrogen.
2. Add approximately 10mL of Hexane into the Turbovap™ tube and concentrate to approximately 1mL final volume.
3. Quantitatively transfer the extract to a 10mL volumetric flask using a pipette and bring to volume using hexane.
4. Transfer the well-mixed sample from the 10mL volumetric flask to a 40mL VOA vial by pouring. Each VOA vial is noted with the test number, sample number and the extraction date.
5. A 2mL amber vial is prepared with the test number, sample number and the extraction date.
6. Using a Hamilton™ syringe, transfer 500µl of the extract into the appropriate 2mL amber vial followed by the addition of 10uL of internal standard.
7. The 40mL VOA vials are placed into archive boxes noting box and row numbers in the appropriate spaces of the extraction logbooks and stored at 4°C (±2°C) in the Sample Prep refrigerator C.
8. Take the extracts to Semi-Vols for analysis.

Method 8310/EPA610 PAH Concentration

EQUIPMENT/APPARATUS

1. 2.0 mL amber crimp top vials
2. Zymark Turbovap™: N_2 blowdown unit
3. Turbovap™ tubes
4. Volumetric Hamilton syringes (Class A), assorted sizes
5. Acrodisc 13mm, Gelman Scientific

REAGENTS

1. Exchange Solvent – Acetonitrile (ACN), pesticide quality or equivalent.
2. Surrogate solutions – Terphenyl-d14 (at 20 ug/mL)1 mL is added to each polynuclear aromatic hydrocarbon samples.
3. Spiking solutions (for MS, MSD, and LCS) – 1 mL of the spike solution is added. The components and concentrations of the spiking solution are listed below. Store at 4°C (± 2°C).

Compound	Concentration
Naphthalene	10 ug/mL
Acenaphthylene	10 ug/mL
Acenaphthene	10 ug/mL
Fluorene	10 ug/mL
Phenanthrene	10 ug/mL
Anthracene	10 ug/mL
Fluoranthene	10 ug/mL
Pyrene	10 ug/mL
Benzo(a)anthracene	10 ug/mL
Chrysene	10 ug/mL
Benzo(b)fluoranthene	10 ug/mL
Benzo(k)fluoranthene	10 ug/mL
Benzo(a)pyrene	10 ug/mL
Indeno(1,2,3-cd)pyrene	10 ug/mL
Dibenzo(a,h)anthracene	10 ug/mL
Benzo(g,h,i)perylene	10 ug/mL

Evaporation, Solvent Exchange and Vialing

1. Place the sample extract, which is in the Turbovap™ tubes, into the Turbovap™ unit (water bath approximately 50°C) and evaporate the solvent to approximately 1mL using a gentle stream of nitrogen.
2. Add approximately 10mL of acetonitrile and reconcentrate to less than 1mL.
3. Remove sample extracts from the Turbovap™.
4. Two sets of amber crimp top vials are prepared. The archive set is prepared by writing the test number, sample number and date. The other set is labeled with the test number, sample number, date and WIS (denoting addition of internal standard).
5. Sample extracts are taken from the Turbovap™ tube using a Hamilton 1mL removable tip syringe.
6. The Turbovap™ tube is then rinsed down with additional quantities of ACN, bringing the volume of the Hamilton syringe with extract to 1mL.
9. The extract is then filtered through a 13 mm Acrodisc by removing the needle from the syringe and connecting it it to the Acrodisc into a 2.0mL prepared stock amber vial.
10. A 250ul portion of the stock extract is then pulled from the archive vial with a 250uL Hamilton syringe and placed in the working 2.0 mL amber vial.
11. A 10ul portion of 8310 internal standard (250ug/mL Carbazole) is added to the working vial using a 10uL Hamilton syringe.

12. Put stock vials into archive boxes, noting box and row numbers in the appropriate spaces of the logbook, make copies of the logbook. Store in the sample prep. refrigerator B @ 4-deg C.
12. Take working extracts to Semi-Vols for analysis.

8310/610-PAH Troubleshooting

1. Water in sample extract - water is present in Tturbovap™ tube prior to concentration. This problem is handled one of two ways depending upon the emulsion present:

   a. Small amount of emulsion present: This problem is handled by taking a Pasteur pipette and removing the emulsion part of the extract off the top and refiltering it back through the original sodium sulfate and filter and rinsing with DCM.

   b. Large amount of emulsion present: the entire sample is re-filtered through a new funnel of DCM rinsed sodium sulfate

   c. If water is present in the concentration tube: The sample extract is filtered through a Pasteur pipette containing glass wool and sodium sulfate. The extract is then brought up to the 1.0mL final volume.

2. If sample is two-phase after concentration:

   a. Add DCM until one phase is obtained and continue adding to the next convenient final volume such as 2.0mL, 5.0mL, 10.0mL etc.

   b. Filter a small portion at least 1/2mL of this concentrate via an acrodisc

   c. Give Semi-Vols a dilution of the extract in ACN, such as 1/5, 1/10 etc. Save the rest of the DCM concentrate as usual in the archives.

3. If a sample looks highly concentrated, viscous black, difficult to handle etc.

   a. Stop the process at the concentration stage. Do not add ACN. Bring the sample final volume up to a convenient level with DCM, such as 1.0mL, 2.0mL, 5.0mL etc.

   b. Filter a small portion at least 1/2mL of this concentrate via acrodisc.

   c. Give Semi-Vols a dilution of the extract in ACN, such as 1/5, 1/10. Save concentrate in archives.

4. DCM flaring (precaution for all HPLC extractions.)

   a. If there is too much DCM in the final extract, there will be unnecessary "flaring" of the chromatogram. After the addition of at least 4mL of ACN, the turbo vap tube should be swirled to ensure that the ACN mixes with the DCM. Then concentrated as usual.

Method 8270/EPA 625 Concentration

EQUIPMENT/APPARATUS

1. Boiling chips solvent rinsed with methylene chloride
2. 2mL amber crimp top vials and caps.

REAGENTS

1. Surrogate Solution: Environmental Express Cat # M0015 @ 100:200ug/mL. There is no preparation necessary for the surrogate solution, the surrogate is ready to use.

2. Spiking Solution: NSI Cat. # Q1141A @ 160 ug/mL. There is no preparation necessary for the spiking solution, the spike is ready to use.
3. Internal Standard: NSI Cat # C-394 @ 2000 ug/mL.

EVAPORATION AND CONCENTRATION

1. Assemble a K-D apparatus by attaching a 10mL receiver tube to a 500mL evaporation flask.
2. Springs or clips should be used to secure the assembly.
3. Add a few clean boiling chips to the receiver tube.
4. Quantitatively transfer the extract from the 500mL Erlenmeyer flask to the K-D apparatus by pouring.
5. Place a methylene chloride rinsed macro-Snyder column on the top of the K-D apparatus.
6. Place the K-D apparatus on the heated steam table (15-20 degC above the boiling point of the solvent) so that the receiver tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. The position and temperature should be optimized to complete the evaporation within 10-20 minutes.
7. Allow the extract to evaporate to approximately 2mL. Remove the apparatus from the steam table and allow it to cool for about 10 minutes in a fume hood.
8. Remove the macro-Snyder column from the receiver tube and place a micro-Snyder column onto the receiver. Evaporate to approximately less than 1mL. Remove the receiver from the water bath and allow to cool in a fume hood for 10min.
9. Using a Hamilton™ syringe, establish a 1mL final volume with methylene chloride and transfer the extract to a labeled 2 mL amber stock vial. Each stock vial is noted with the test number, sample number and the extraction date.
   a) If the extract does not easily evaporate to a 1mL final volume, contact the Sample Prep Team Leader or Section Leader. A larger final volume may be necessary.
10. Transfer 500 (L into a second 2mL amber vial labeled with the test number, sample number and the extraction date and WIS (with internal standard). Add 10 (L of internal standard into the vial.
11. The WIS vial is given to the Semi-Vols for analysis.
15. The stock vials are placed into archive boxes noting box and row numbers in the appropriate spaces of the extraction logbooks and stored at 4°C (±2°C) in the Sample Prep refrigerator B.

TCLP 1311/8270/625

1. TCLP extraction is prepared by Method 1311.

2. One TCLP must be accompanied by a sample spike. 1L of TCLP extract is split into two equal 500mL portions. One 500mL portion for the sample, and the other 500mL portion for the sample spike. If less volume is available, divide the total volume equally.

3. For TCLP samples add 250 µL of 8270 BNA Spike @ 160ug/ml to one aqueous sample after splitting the sample into equal volumes. Note: the Maximum Volume for TCLP is 500ml.

CALCULATIONS

You will need to be familiar with calculating spike, surrogate, and reagent concentrations. Please have your section supervisor peer check your calculation prior to making any solutions. Never assume the last analyst made the solution correctly. Double check their calculations as well.

REVIEW/VALIDATION

Review of extraction logbook before release is the responsibility of the team leader in the extraction area or designee. The logbook will be reviewed for completeness, correctness, and then signed before copies are made for the appropriate analytical area.

DOCUMENTATION

The analyst(s) performing the work will make the appropriate documentation. The analyst is responsible for finding a peer to witness the addition of spike to the QC samples. The spike witness must sign off on the extraction log.

Any difficulties encountered during sample preparation will be noted on the extraction log. Examples of events that should be documented are emulsions, loss of sample or extract, odor and difficulty concentrating extract. Such notes are useful if and when corrective action is necessary.

Per laboratory policy, any changes to information in the extraction log book should be made by drawing single-line through incorrect information and writing correct information The person making change will then initial and date the change.

HEALTH AND SAFETY

Methylene chloride is a hazardous chemical and should be handled with care. Methylene chloride should always be used in a hood. Laboratory safety equipment is provided to minimize contact. Appropriate protective equipment and clothing must be used under the assumption that all samples and chemicals are potentially hazardous. Safety glasses are required in the prep building at all times and gloves and lab coats are highly recommended. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

POLLUTION AND PREVENTION

Pollution and Prevention encompasses any technique that reduces or eliminates the quantity and/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

For more information about pollution prevention consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477

WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable Federal, state, and local rules and regulations. 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 sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477

REFERENCES

- Guidance for the Preparation of Standard Operating Procedures for Quality-Related Documents, EPA QA/G-6, November 1995.
- Test Methods for Evaluating Solid Waste, SW-846, Update III, December 1996, Method 3510,
- GPO # 955-001-00000-1
- *Methods for Chemical Analysis of Water and Wastes,* EPA 600/4-79-020, March 1983. Method 608
- Test Methods for *Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 8082
- *Methods for Chemical Analysis of Water and Wastes,* EPA 600/4-79-020, March 1983. Method 8141
- Test Methods for *Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 8310
- Test Methods for *Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 8081
- *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods,* SW-846 (3rd Edition, Update III, Dec. 1996) Methods 8000B, 8270C.
- 40 CFR Part 136, Appendices A-D. EPA Method 625

- Florida Department of Environmental Protection, Method for Determination of Petroleum Range Organics (Method # FL-PRO), Revision1, November 1, 1995.
- SOP00040-*QA, Rules for Documentation*

TABLE 1: SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

	Initial Extraction pH	Secondary Extraction pH	Analysis Solvent Exchange	Cleanup Solvent Exchange	Cleanup Volume of Extract (ml)	Analysis Volume of Extract (ml)
608/8081,8082	5-9	none	hexane	hexane	10.0	10.0
614/8141	as received	none	hexane	hexane	10.0	10.0
625/8270[ab]	<2	>12	none	---	---	1.0
610/8310	5-9	none	acetonitrile	---	---	1.0
Fl Pro	<2	none	none	----	2.0	2.0
8015 DRO	5-9	none	none	----	----	1.0

[a]The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to method 3600 for guidance on the cleanup procedures available if required.

[b]Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes.

PEL Laboratories, Inc.

PEL Laboratories, Inc.- Standard Operating Procedure

Sample Preparation: SW-846 3550B Sonication

APPROVED:

Sample Prep.Team Leader Date

Sample Prep Section Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories to isolate organic compounds from soil/sediment samples by sonication for methods: SW-846 3550B. This SOP applies specifically to the following methods: 608/8081/8082, 610/8310, 614/8141, FL PRO and 8015 DRO.

Method 3550 is a procedure for extraction of non-volatile and semi-volatile organic compounds. This method applies to the extraction of solids such as soils, sludge's, and wastes. It utilizes the technique of ultrasonic extraction. The sonication process ensures intimate contact of the sample matrix with the extraction solvent.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the laboratory technician, and providing adequate explanation of the material contained. This SOP is restricted to use by or under the supervision of trained technicians. Each technician must demonstrate the ability to generate acceptable results with this SOP.

The following methods require special instructions or more in-depth descriptions:

Refer to SOP00023-P and SOP00024-P for TX1005 extraction techniques.

Refer to SOP00088-P for 615/8151 extraction techniques.

Refer to SOP00076-P for 8330 extraction techniques.

The specificity of GC/MS may make cleanup of 625/8270 extracts unnecessary. Refer to method 3600 for guidance on the cleanup procedures available if required.

Please refer to the following PEL SOPs for guidance prior to extracting:

Refer to the standards table SOP00089-P for spike, standard and surrogate preparation.

Refer to SOP00084-P for general extraction/QA procedures.

QA/QC REQUIREMENTS

This SOP was written to conform with all QA/QC criteria described in the following methods: SW-846 3550B.

Contaminants in solvents, reagents, glassware, and other sample processing may cause method interferences. Method blanks are prepared with field samples to demonstrate that the laboratory process is free of such contaminants. Purified Ottawa sand is used for the method blank.

Glassware must be scrupulously cleaned. (See SOP00072-P)

Surrogates are added to all samples (including QC samples) immediately before extraction to monitor the success of each sample preparation. Poor surrogate recovery requires investigation. Re-extraction is the logical corrective action if sufficient raw sample is available and if the holding time has not expired. Where no method or program limits are mandated, acceptance limits will be determined using laboratory data or project specified requirements.

Matrix spikes and matrix spike duplicates (MS/MSD) are prepared by spiking an aliquot of an environmental sample with known quantities of the method analytes. If no spiking requirements are communicated, spiking will be performed as specified in applicable method. The MS/MSD is analyzed exactly like a sample, and its purpose is to determine whether sample matrix contributes bias to the analytical results by determining the accuracy of each and the precision associated with the spikes. The background concentrations of the analytes in the native sample must be determined in a separate aliquot and the measured values in the MS/MSD corrected for native concentration. If the client has not identified samples to be spiked, baked Ottawa sand will be used for spiking. The laboratory will prepare MS/MSD at a frequency of 1 set per 20 samples. **For AFCEE**, the MS/MSD count as samples in the batch of 20. MS/MSD results will be compared to established laboratory limits for acceptability. Since the native matrix may have a detrimental effect on accuracy and precision, a LCS is prepared with every MS/MSD. If MS/MSD does not meet acceptance criteria and the associated LCS is acceptable, matrix effect is assumed. Where no method or program limits are mandated, generic limits will be used until in-house limits are determined using laboratory data.

A laboratory control sample (LCS) is prepared by spiking representative target compounds into a blank matrix (Ottawa Sand). The LCS is processed through the same extraction, concentration, and cleanup procedures as the samples. Where no method or program limits are mandated, generic limits will be used until in-house limits are determined using laboratory data.

EQUIPMENT/APPARATUS

1. 250 ml Beakers
2. Sonicator
3. Filter Paper – Whatman # 41
4. Glass Wool
5. Funnels
6. Top loader balance
7. Steam table: Heated with concentric ring cover.
8. Hamilton (Class A) volumetric syringes, assorted sizes.
9. 250mL, 500mL Erlenmeyer Flask
10. Turbovap™ tubes
11. Zymark Turbovap™: N_2 blowdown unit
12. K-D Apparatus
13. Condenser Tubes
14. 3-ball Macro-snyder
15. 2-ball Micro-snyder

REAGENTS

1. Solvents

a) Extraction Solvent – Methylene chloride (DCM), pesticide quality or equivalent.
b) Extraction Solvent - Acetone, pesticide quality or equivalent.

2. Sodium Sulfate (Na_2SO_4): Granular, anhydrous, Purified at 160°C for ~12 hours, cooled, and stored in glass jars.

PROCEDURE

Characterize samples – identify and record the following characteristics:

a) Color
b) Odor
c) Sediment
d) Sample Date

Extraction

1. Prepare (rinse) all glassware with the extraction solvent, generally 1:1 methylene chloride/acetone.
2. Weigh 33 grams of sample into a beaker. (FL-PRO use 25.0 grams of sample)
   ***Note: all soils for AFCEE must be weighed to account for the percent solids.**
3. Add enough sodium sulfate to the sample until it is free flowing. Generally, this is about 60 grams.
4. The blank and quality control are represented by 33.0 g Ottawa sand in the prepared beakers.
5. Add surrogate to all quality control and samples.
6. Add spiking solutions to all quality control where applicable.
7. Add 60 ml of a 1:1 DCM and Acetone mixture
8. Place sample beaker into sonicator booth, ensuring that the tip of the horn is in under the solvent layer, but above the sample layer.
9. Sonicate for three minutes with output control set at four, mode switch on pulse, and percent duty set at 50%.
10. Decant and filter the extract through either filter paper or glass wool (method dependent) and a small amount of sodium sulfate contained in the funnel (generally, about 1 g).
11. Rinse sodium sulfate thoroughly with solvent.
12. Repeat sonication process two more times using a fresh 60 ml of solvent.
13. Proceed to applicable sample concentration method.

Addendums

Method 8015-Dro Concentration

EQUIPMENT/APPARATUS

1. 500mL KD Receiving flasks
2. 10mL Concentrator tubes
3. 3-ball Macro-Snyder column
4. 2-ball Micro-Snyder column
5. Boiling chips solvent rinsed with methylene chloride
6. Steam table (heated), with concentric ring cover
7. 2mL amber crimp top vials
4. Pasteur pipettes, disposable, borosilicate glass
5. Hamilton (Class A) 1.0mL volumetric syringe
6. 250mL Erlenmeyer flask

REAGENTS

1. Surrogate stock solution: o-terphenyl(OTP), NSI 1341 @ 2000ug/mL. See standards table for preparation of working surrogate solution.
2. Raw Diesel fuel 100% pure. See standards table for preparation of working spike solution.

Evaporation

1. Add a boiling chip to the K-D and attach a three ball macro-snyder column to the top. Place the K-D apparatus on the steam table (15-20-deg C above the boiling point of the solvent) and cook down until the extract volume is less than 4mLs. Remove from the steam table and allow to cool at least 10 minutes.
2. Prepare the sample for micro-cook down by attaching a two-ball micro-snyder to the concentrator tube. Place the sample back on the steam table and cook down to a volume of less than 1mL. Allow the sample to cool for at least 10 minutes. Proceed to vialing.
3. Draw out exactly 1mL of sample from the concentrator tube (DCM can be used to bring to volume if needed) utilizing a 1mL Hamilton syringe. Place the extract in a 2mL amber stock vial labeled with test, project number, sample number and extraction date. From the stock vial, draw out 500uL and place in another labeled 2mL amber vial to go to Semi-Vols for analysis.

Method 8081/EPA 608 concentration

EQUIPMENT/APPARATUS

1. Turbovap™ tubes
2. Pipettes: disposable, borosilicate glass
3. 10mL volumetric flasks
4. Hamilton Class A Volumetric syringes
5. 40mL VOA vials
6. 2mL amber vials with crimp tops
7. Zymark Turbovap™

REAGENTS

1. Exchange Solvent - Hexane, pesticide quality or equivalent
2. Surrogate stock solution - Ultra Scientific Cat. #ISM-320@200(g/mL. See standards table for preparation of Working Surrogate solution.
3. Spike stock solution – Ultra Scientific OrganoChloride Pesticides Mixture Cat. #US-127@2000(g/mL. See standards table for preparation of Working Spike solution.
4. Internal Standard stock solution – Ultra Scientific Pentachloronitrobenzene

Evaporation and Solvent Exchange

1. Place the Turbovap™ tubes into the Turbovap™ unit (water bath at 50°C) and evaporate the solvent to approximately 1mL using a gentle stream of nitrogen.
2. Add approximately 10mL of Hexane into the Turbovap™ tube and concentrate to approximately 1mL final volume.
3. Quantitatively transfer the extract to a 10mL volumetric flask using a pipette and fill to volume with Hexane.
4. Transfer the well-mixed sample from the 10mL volumetric flask to a 40mL VOA vial by pouring. Each VOA vial is noted with the test number, sample number and the extraction date.
5. A 2mL amber vial is prepared with the test number, project number, sample number and the extraction date.
6. Using a Hamilton™ syringe, transfer 500µL of the extract into the appropriate 2mL amber vial followed by the addition of 5uL of internal standard.
7. The 40mL VOA vials are placed into archive boxes noting box and row numbers in the appropriate spaces of the extraction logbooks and stored at 4°C (±2°C) in the Sample Prep refrigerator C.
8. Take the extracts to Semi-Vols for analysis.

TCLP 1311/8081

1.TCLP extraction is prepared by Method 1311.

2. One TCLP must be accompanied by a sample spike. 1L of TCLP extract is split into two equal 500mL portions. One 500mL portion for the sample, and the other 500mL portion for the sample spike. If less volume is available, divide the total volume equally.

3. 8081 TCLP spike consists of the regular pesticide spike, refer to SOP00089-P.

4. When there are only TCLP samples are present per analytical batch, the extractionist only needs to do a blank, LCS (with normal spike), sample, and sample TCLP spike. No MS/MSD is required.

Method 8082-PCB Concentration

EQUIPMENT/APPARATUS

1. Turbovap™ tubes
2. Pipettes: disposable, borosilicate glass
3. 10mL volumetric flasks
4. Hamilton Class A Volumetric syringes
5. 40mL VOA vials
6. 2mL amber vials with crimp tops
8. Zymark Turbovap™

REAGENTS

1. Exchange Solvent: Hexane, pesticide quality or equivalent.
2. Surrogate stock solution: Ultra Scientific pesticide surrogate standard spiking solution Cat. # ISM-320 @ 200-ug/mL. See working standards table for preparation of working surrogate solution.
3. Spiking stock solution: Ultra Scientific Aroclor 1016 solution Cat. # pp-282 @ 100-ug/mL and Ultra Scientific Aroclor 1260 solution Cat. # pp-361 @ 100ug/mL. See working standards table for preparation of working spiking solution.

EVAPORATION AND SOLVENT EXCHANGE

1. Place the Turbovap™ tubes into the Turbovap™ unit (water bath at 50°C) and evaporate the solvent to approximately 1mL using a gentle stream of nitrogen.
2. Add approximately 10mL of Hexane into the Turbovap™ tube and concentrate to approximately 1mL final volume.
3. Quantitatively transfer the extract to a 10mL volumetric flask using a pipette and bring to volume using hexane.
4. Transfer the well-mixed sample from the 10mL volumetric flask to a 40mL VOA vial by pouring. Each VOA vial is noted with the test number, sample number and the extraction date.
5. A 2mL amber vial is prepared with the test number, sample number and the extraction date.
6. Using a Hamilton™ syringe, transfer 500µl of the extract into the appropriate 2mL amber vial.
7. The 40mL VOA vials are placed into archive boxes noting box and row numbers in the appropriate spaces of the extraction logbooks and stored at 4°C (±2°C) in the Sample Prep refrigerator C.
8. Take the extracts to Semi-Vols for analysis.

METHOD FL PRO CONCENTRATION

EQUIPMENT/APPARATUS

1. 500mL KD Receiving flasks
2. 10mL Concentrator tubes
3. 3-ball Macro-Snyder column
4. 2-ball Micro-Snyder column
5. Boiling chips solvent rinsed with methylene chloride
6. Steam table (heated), with concentric ring cover
7. 2mL amber crimp top vials
8. Pasteur pipettes, disposable, borosilicate glass
9. Hamilton (Class A) 1.0mL volumetric syringe
10. 250mL Erlenmeyer flask
11. 40mL clear VOA vials

REAGENTS

1. Surrogate solutions:
   a. o-terphenyl (OTP), NSI 1341 @ 2000 µg/mL
   b. Nonatriacontane (C-39), NSI 1339 @ 6000 µg/mL
2. Spike solution: NSI c-443 @ 2000 ug/ml, encompassing Petroleum Hydrocarbon components C8-C40.
3. Silica gel-chromatographic (100-200 mesh)

Concentration

1. Place a three-ball macro Snyder column on the K-D receiving flask.
2. Place the K-D flask on the heated water bath 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. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood.
3. When the apparent volume of the liquid appears to be less than 4mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.
4. Remove the K-D receiving flask, place a micro Snyder column onto the concentrator tube, and concentrate to an apparent volume of less than 2mL by cooking it down on the water bath. Let cool again.

SILICA GEL CLEAN-UP & VIALING (MANDATORY)

1. Draw out exactly 2mL of sample from concentrator tube using a volumetric syringe (DCM can be used to bring to volume if needed) and place in a previously prepared VOA vial containing 0.3 g of silica gel. Shake the mixture gently for 30 seconds and allow to settle out. (The purpose of the silica gel is to pull out any oils that may cause interferences with the analysis).
2. Draw out the extract from each VOA vial using disposable glass pipettes and place into a 2mL amber crimp top vial labeled with the test, project and sample number, plus the date. Using another disposable glass pipette, draw out at least 500µl of the sample and place it into a duplicate amber crimp top vial.
3. The first set of vials are placed into archive boxes noting box and row numbers in the appropriate spaces of the extraction logbooks and stored at 4-deg C (+/-2-deg C) in the sample prep. refrigerator C.
4. The second set of vials is taken to Semi-Vols for analysis.

EQUIPMENT/APPARATUS

1. Turbovap™ tubes
2. Pipettes: disposable, borosilicate glass
3. 10mL volumetric flasks
4. Hamilton™ Gastight® syringes
5. 40mL VOA vials
6. 2mL amber vials with crimp tops
7. Zymark Turbovap™

REAGENTS

1. Exchange Solvent: Hexane, pesticide quality or equivalent
2. Surrogate solution- Ultra Scientific Cat. # M-1428 @ 500ug/mL. See working standards table for preparation.
3. Spiking solution- Ultra Scientific Cat. 3 SPM-614 @ 200ug/mL. No preparation is necessary for spiking solution, the spike is ready to use.
4. Internal standard- Ultra Scientific PPS-350 @ 1000ug/mL.

Evaporation and Solvent Exchange

1. Place the Turbovap™ tubes into the Turbovap™ unit (water bath at 50°C) and evaporate the solvent to approximately 1mL using a gentle stream of nitrogen.
2. Add approximately 10mL of Hexane into the Turbovap™ tube and concentrate to approximately 1mL final volume.
3. Quantitatively transfer the extract to a 10mL volumetric flask using a pipette and bring to volume using hexane.
4. Transfer the well-mixed sample from the 10mL volumetric flask to a 40mL VOA vial by pouring. Each VOA vial is noted with the test number, sample number and the extraction date.
5. A 2mL amber vial is prepared with the test number, sample number and the extraction date.
6. Using a Hamilton™ syringe, transfer 500µl of the extract into the appropriate 2mL amber vial followed by the addition of 10uL of internal standard.
7. The 40mL VOA vials are placed into archive boxes noting box and row numbers in the appropriate spaces of the extraction logbooks and stored at 4°C (±2°C) in the Sample Prep refrigerator C.
8. Take the extracts to Semi-Vols for analysis.

Method 8310/EPA 610 PAH Concentration

EQUIPMENT/APPARATUS

1. 2.0 mL amber crimp top vials
2. Zymark Turbovap™: N_2 blowdown unit
3. Turbovap™ tubes
4. Volumetric Hamilton syringes (Class A), assorted sizes

5. Acrodisc 13mm, Gelman Scientific

REAGENTS

1. Exchange Solvent – Acetonitrile (ACN), pesticide quality or equivalent.
2. Surrogate solutions - Terphenyl-d14 (at 20 ug/mL) 1mL is added to each polynuclear aromatic hydrocarbon samples.
3. Spiking solutions (for MS, MSD, and LCS) – 1 mL of the spike solution is added. The components and concentrations of the spiking solution are listed below. Store at 4°C (± 2°C).

Compound	Concentration
Naphthalene	10 ug/mL
Acenaphthylene	10 ug/mL
Acenaphthene	10 ug/mL
Fluorene	10 ug/mL
Phenanthrene	10 ug/mL
Anthracene	10 ug/mL
Fluoranthene	10 ug/mL
Pyrene	10 ug/mL
Benzo(a)anthracene	10 ug/mL
Chrysene	10 ug/mL
Benzo(b)fluoranthene	10 ug/mL
Benzo(k)fluoranthene	10 ug/mL
Benzo(a)pyrene	10 ug/mL
Indeno(1,2,3-cd)pyrene	10 ug/mL
Dibenzo(a,h)anthracene	10 ug/mL
Benzo(g,h,i)perylene	10 ug/mL

Evaporation, Solvent Exchange and Vialing

1. Place the sample extract, which is in the Turbovap™ tubes, into the Turbovap™ unit (water bath approximately 50°C) and evaporate the solvent to approximately 1mL using a gentle stream of nitrogen.
2. Add approximately 10mL of acetonitrile and reconcentrate to less than 1mL.
3. Remove sample extracts from the Turbovap™.
4. Two sets of amber crimp top vials are prepared. The archive set is prepared by writing the test number, sample number and date. The other set is labeled with the test number, sample number, date and WIS (denoting addition of internal standard).
5. Sample extracts are taken from the Turbovap™ tube using a Hamilton 1mL removable tip syringe.
6. The Turbovap™ tube is then rinsed down with additional quantities of ACN, bringing the volume of the Hamilton syringe with extract to 1mL.
7. The extract is then filtered through a 13 mm Acrodisc by removing the needle from the syringe and connecting it to the Acrodisc into a 2.0mL prepared stock amber vial labeled with the test, project number, sample number and extraction date.
8. A 250ul portion of the stock extract is then pulled from the archive vial with a 250uL Hamilton syringe and placed in the working 2.0 mL amber vial.
9. A 10ul portion of 8310 internal standard (250ug/mL Carbazole) is added to the working vial using a 10uL Hamilton syringe.

10.Put stock vials into archive boxes, noting box and row numbers in the appropriate spaces of the logbook, make copies of the logbook. Store in the sample prep. refrigerator B @ 4-deg C.

11.Take working extracts to Semi-Vols for analysis.

8310-PAH Troubleshooting

1. If sample is two-phase after concentration:
   a. Re-extract using a lesser amount of soil.
   b. Add DCM until one phase is obtained and continue adding to the next convenient final volume level such as 2mL, 5mL, 10mL etc.
   c. Filter a small portion at least 1/2mL of this concentrate via an acrodisc
   d. Give Semi-Vols a dilution of the extract in ACN, such as 1/5, 1/10 etc. Save the rest of the DCM concentrate as usual in the archives.
2. If a sample looks highly concentrated, viscous, black, difficult to handle etc.
   a. Stop the process at the concentration stage. Do not add ACN. Bring the sample final volume up to a convenient level with DCM, such as 1mL, 2mL, 5mL etc.
   b. Filter a small portion at least 1/2mL of this concentrate via acrodisc.
   c. Give Semi-Vols a dilution of the extract in ACN, such as 1/5, 1/10. Save concentrate in archives.
3. DCM flaring (precaution for all HPLC extractions.)
   a. If there is too much DCM in the final extract, there will be unnecessary "flaring" of the chromatogram. After the addition of at least 4mL of ACN, the turbovap tube should be swirled to ensure that the ACN mixes with the DCM. Then cook down is continued as usual.

CALCULATIONS

You will need to be familiar with calculating spike, surrogate, and reagent concentrations. Please have your section supervisor peer check your calculation prior to making any solutions. Never assume the last analyst made the solution correctly. Double check their calculations as well.

REVIEW/VALIDATION

Review of extraction logbook before release is the responsibility of the extraction team leader in the extraction area or designee. The logbook will be reviewed for completeness, correctness, and then signed before copies are made for the appropriate analytical area.

DOCUMENTATION

The analyst(s) performing the work will make the appropriate documentation. The analyst is responsible for finding a peer to witness the addition of spike to the QC samples. The spike witness must sign off on the extraction log.

Any difficulties encountered during sample preparation will be noted on the extraction log. Examples of events that should be documented are emulsions, loss of sample or extract, odor and difficulty concentrating extract. Such notes are useful if corrective action is necessary.

Per laboratory policy, any changes to information in the extraction log book should be made by drawing single-line through incorrect information and writing correct information The person making change will then initial and date the change.

HEALTH AND SAFETY

Methylene chloride is a hazardous chemical and should be handled with care. Methylene chloride should always be used in a hood. Laboratory safety equipment is provided to minimize contact. Appropriate protective equipment and clothing must be used under the assumption that all samples and chemicals are potentially hazardous. Safety glasses are required in the prep building at all times and gloves and lab coats are highly recommended. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

POLLUTION AND PREVENTION

Pollution and Prevention encompasses any technique that reduces or eliminates the quantity and/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

For more information about pollution prevention consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477

WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable Federal, state, and local rules and regulations. 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 sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477

REFERENCES

- Guidance for the Preparation of Standard Operating Procedures for Quality-Related Documents, EPA QA/G-6, November 1995.
- Test Methods for Evaluating Solid Waste, SW-846, Update III, December 1996, Method 3550, GPO # 955-001-00000-1
- Test Methods for *Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 8082
- Test Methods for *Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 8141
- Test Methods for *Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 8310
- Test Methods for *Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 8081

- Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW-846 (3rd Edition, Update III, Dec. 1996) Methods 8000B.
- Florida Department of Environmental Protection, Method for Determination of Petroleum Range Organics (Method # FL-PRO), Revision1, November 1, 1995.
- SOP 00035-WC, % Moisture.
- SOP 00040-*QA Rules for Documentation*

PEL Laboratories, Inc. Standard Operating Procedure

Sample analysis: 625/8270C GC/MS Semi-Volatile Organics

APPROVED:

Semi-Volatiles Section Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. to analyze water, soil, waste and leachate sample extracts for selected semi-volatile compounds by using gas chromatography / mass spectrometry (GC/MS) techniques. This SOP was written to conform to all quality assurance/quality control (QA/QC) criteria described in EPA Method 625 and SW846-8270. The intention of this SOP is to allow individual or simultaneous analysis of samples by the EPA methods listed above for water samples (EPA method 625 is a guideline for waters only). Method specific QA/QC requirements are listed in the appropriate sections, tables, and where applicable throughout this SOP.

This SOP presupposes that the analyst has working knowledge and experience in the operation of GC/MS equipment and a GC/MS data system. Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Managers are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

The standard reporting list of compounds for referenced methods is located in Table 1.

SUMMARY OF THE METHOD

Samples are extracted by one of three techniques:

- Separatory Funnel (Method SW846-3510). A measured volume of sample, usually one liter, is placed into a separatory funnel, the pH adjusted if necessary, and serially extracted (three times) with Methylene Chloride. Usually an additional pH adjustment is required, the sample is serially re-extracted (three times) at the second pH with fresh Methylene Chloride. Refer to extraction SOP 3510.
- Sonication (Method SW846-3550). A measured sample, usually 33 grams, is mixed with anhydrous sodium sulfate and serially extracted three times with 1:1 Methylene Chloride and Acetone. The extract is separated from the sample by filtration. Refer to extraction SOP 3550.
- ASE (Method SW846-3545). A measured sample, usually 30 grams, is mixed with anhydrous sodium sulfate and extracted on the accelerated solvent extractor. Refer to extraction SOP 3545.

After sample preparation has been completed, 500 ul of the extract is spiked with internal standards and injected directly into the GC/MS. The sample extract is flash vaporized and swept on to the column by means of a split/splitless injector. The semi-volatile components are thus transferred onto a chromatographic column, which is temperature programmed to separate the compounds. As the compounds elute from the GC column, they pass through a heated transfer line into the mass spectrometer. The compounds are ionized by electron impact, and the ion fragments detected by an electron multiplier. The GC/MS data system identifies the compounds by characteristic spectra and quantifies them via the internal standard method.

INTERFERENCES

Method interference may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in gas chromatograms. Method blanks are prepared with field samples to demonstrate reagents and glassware are free of interferences. The presence of high levels of phthalates in samples or blanks may be indicative of method interferences, and such occurrences should receive further investigation.

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source. Viscous or sediment laden extracts should be diluted prior to analysis to extend column lifetime.

Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. To reduce carryover, the sample syringe must be rinsed out between samples with methylene chloride. If carryover is suspected, the impacted sample(s) must be reanalyzed.

QA/QC REQUIREMENTS

1. Please review the Qualitative and Quantitative sections of this SOP for possible additional requirements.
2. Table 2 lists the characteristic ions for regular target analytes, surrogates, and internal standards analyzed using this SOP.
3. Instrument calibration
   a. Prior to initiating any data collection activities involving samples or standards, it is necessary to establish that the GC/MS system meets the instrument performance criteria. The purpose of this instrument performance check is to assure correct mass calibration, mass resolution, and mass transmission. This is accomplished through the analysis of Decafluorotriphenylphosphine (DFTPP). The key ions produced during the analysis of DFTPP, and their respective ion abundance criteria are given in Table 3.
   b. Initial calibration curve consists of five points, at a minimum (PEL currently uses a six point calibration, allowing the analyst to "drop" a standard in the curve if necessary to achieve linearity). The low standard in the curve should be left in if at all possible. The curve will be analyzed to determine the linearity of response. Once the curve has been verified, analysis can proceed.
   c. A calibration standard from a source different from that used to obtain the initial calibration curve will be analyzed immediately after the calibration curve as an independent verification on the accuracy of the calibration standards.
   d. A continuing calibration standard will be analyzed at the beginning of each 12-hour analytical sequence, prior to the acquisition of any samples.
   e. Initial and continuing calibration criteria are listed Table 4.
      i. All listed compounds must meet the appropriate minimum relative response factor (RRF) and percent relative standard deviation (%RSD) criteria listed for the calibration to be considered valid.
      ii. For continuing calibrations, the %Difference (%Diff or %D) for each target compound may not exceed the listed value.
      iii. For continuing calibration verification the average %RSD and %D can be used not to exceed 15% for RSD and 20% for %D. Some clients and/or project instructions dictate other limitations i.e. no more than 5% of the analytes may exceed limits and none shall exceed 40%.
4. Blanks
   a. Method blanks are used to verify the absence of contamination in the laboratory at the time during which samples were prepared and analyzed. Each batch of up to 20 field samples prepared by solvent extraction must have an associated method blank. (AFCEE batches are 18 field samples.)
   b. For the purposes of this SOP, an acceptable method blank must be less than or equal to the RL.
   c. If a method blank exceeds the limits for contamination, the analytical system is considered to be out of control. The source of the contamination must be investigated and appropriate corrective actions taken and documented before further sample analyses can proceed.
   d. Blank contamination should be confirmed by re-prepping and re-analyzing the blank in question.
5. Laboratory Control Samples (LCS) - An LCS is a reagent blank spiked with internal standards, surrogates, and project specific target compounds. A LCS is prepared and extracted with a batch of samples, and generally analyzed following the reagent (water or Ottawa sand) MS/MSD samples. LCSs will be evaluated using historical in-house limits or 70-130% until there are at least 20 data points to establish such limits.

RPDs between LCS duplicates must be less than 25% until sufficient data points can be generated to establish historical in-house limits.

6. Matrix Spike/Matrix Spike Duplicate (MS/MSD).
   a. For every batch of samples, at least one sample must be spiked in duplicate. For the purposes of this SOP, a batch of samples is any number of samples up to 20 of the same matrix that were extracted together. (AFCEE batches are 18 field samples.)
   b. The spike level is 40 µg/L for the base neutral compounds and 40 µg/L for the acidic compounds. *Special requirements may apply regarding spiking levels for samples used in support of compliance monitoring or samples that have high levels of target analytes.*
   c. The quality control limits for recovery and relative percent difference are given in the current PEL Quality Manual. Historical limits are used for the evaluation of EPA 625 and SW-846 methods.
7. Surrogate spike.
   a. Each sample analyzed will be spiked with surrogate compounds to monitor sample specific analytical performance. Spiking levels are 100 µg/L for the base neutral compounds and 200 µg/L for the acidic compounds
   b. Surrogate recoveries must be within the range as stated for each method, or within the limits specified by special project instruction. (PEL currently uses the method's published limits unless otherwise specified. Historical limits are calculated and filed for reference.)
   c. If any sample exhibits surrogate recoveries outside these limits, the sample must be re-analyzed (and re-extracted if applicable). If the problem persists, the reported values must be flagged as estimated. If the sample is part of a level III project the analyst must note the corrective action taken in the case narrative when necessary.
8. Holding times. All sample extracts must be analyzed within 40 days after the date sample extraction began.
9. For level 1 projects citing a method, the method requirements have priority. However, when samples are analyzed under a project specific QAPP (i.e., AFCEE) the QA/QC criteria of that QAPP and its specific corrective actions listed have precedence for those select samples.

EQUIPMENT/APPARATUS

1. Gas Chromatograph (GC) – HP 5890 and 6890 Analytical systems equipped with EPC that have all required accessories for proper operation. The capillary column is directly coupled to the GC/MS source.
2. Mass spectrometer (MS) – (HP 5972 and 5973 utilized) must be capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng of DFTPP is analyzed.
3. GC/MS interface - any GC to MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes of interest and achieves all acceptance criteria may be used.
4. Data System - A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage, on machine-readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass, and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. In addition, the most recent version of the EPA/NIH Mass Spectral Library should be available. The software system must be capable of flagging all data files that have been edited manually by laboratory personnel.
5. Gas Chromatographic Columns. A typical column used is the HP-5MS.
6. Autosampler 2mL amber vials/crimp tops
7. Crimper and Decrimper
8. Syringes, gas tight, various sizes
9. Volumetric flasks, with ground glass stoppers
10. See the *GC/MS Maintenance* SOP for guidance on preventative and routine maintenance of equipment.

REAGENTS

1. Methylene chloride, pesticide grade.
2. Standards. All Semivolatile standards must be stored separately from samples. Store stock or working standards in Teflon™-sealed screw-cap amber vials at 4°C.

a. Stock Standard Solutions. Stock standard solutions are high concentration solutions used to prepare intermediate or working standards that will be used. Expiration of stock standard solutions are as followed; six months after opening, the expiration on the ampule as listed by the manufacturer, or if no expiration listed, one year after receipt in the laboratory. All standards will be labeled with their SV# (This number is found in the SV- book, which numerically numbers all standards. It includes the manufacturer, concentration, and received date for stock standards used. For working standards, it lists the stock standards used, the diluent, how much stock standard to use, final volume and final concentration.), name of the standard, concentration and date.

b. Working Standard Solutions. Using the stock standard solutions, prepare the following working standard solutions by making appropriate dilutions in Methylene chloride. Working standard solutions have expiration dates of six months after the preparation date but are usually prepared weekly. All standards will be labeled with their SV#, name of the standard and concentration.

   i. Calibration Standards (**STD**)- Combine all target analytes, including surrogates, in a methylene chloride solution. Prepare calibration standards at the following concentrations for each target compound and surrogate: 10 µg/mL, 20 µg/mL, 45 µg/mL, 60 µg/mL, 75 µg/mL, and 100 µg/mL. The compounds included in each standard are method specific - consult Tables 1-3 for specific compounds required. Calibration standards are stored in the freezer at –10°C to –20°C.

   ii. Secondary standard (**SECSTD**) – A stock standard is obtained from a different source other than the calibration standards, and a working level standard is prepared at mid-cal range(45 ug/mL).

   iii. Internal standards (**IS**) - 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12} and Perylene-d_{12} is at a working concentration of 2,000 µg/mL.

   iv. GC tuning compound- Decafluorotriphenylphosphine (**DFTPP**) - Prepare a solution of DFTPP in methylene chloride solution at 25 µg/mL. Store at 4°C in refrigerator E.

   v. See Appendix B for regular 8270 standard preparation.

PROCEDURE

1. Operating Conditions
   a. Gas Chromatograph - The instrumental operating conditions will be appropriate for the columns being used. The laboratory will maintain documentation regarding the columns and analysis conditions actually employed in that laboratory.
   b. Mass Spectrometer–Actual temps are listed. (The suggested operating conditions are listed in Table 5.)
      i. Electron Energy - 70 volts (nominal)
      ii. Mass Range - 35 - 500 amu
      iii. Scan time - to give at least five scans per peak, not to exceed 1 second per scan for capillary column.
      iv. Injection Port Temperature-250°C
      v. Transfer Line Temperature - 300°C
      vi. Source Temperature – 300°C.

2. Analytical sequences.
   a. All analyses in an analytical sequence must be started within 12-hour blocks of time in order to be valid which begins at the time of injection of DFTPP and ends after exactly twelve (12:00) hours have elapsed according to the system clock.
   b. The analysis of DFTPP must pass all criteria set forth in Table 3.
   c. Following the valid DFTPP run, the instrument must be calibrated using a multi-point calibration curve (initial calibration) or the calibration verified using a single point continuing calibration standard. Initial and continuing calibration must pass all criteria set forth in this SOP before sample analysis can continue.
   d. Following a successful calibration or calibration check, the analyst may analyze as many sample extracts - including QC - as can be accommodated within the 12-hour period following the injection of DFTPP.
   e. **Any analysis started after the 12-hours elapse is invalid and may not be reported.**

3. DFTPP Calibration
   a. Requirements
      i. Prior to initiating any data collection activities involving samples, blanks, or standards, it is necessary to establish that the GC/MS system meets the instrument performance criteria. The purpose

of this instrument performance check is to assure correct mass calibration, mass resolution, and mass transmission. This is accomplished through the analysis of DFTPP. The key ions produced during the analysis of DFTPP, and their respective ion abundance criteria are given in Table 5.

ii. The instrument must be calibrated using the same mass spectrometer instrument conditions that are used to analyze the samples.

b. Procedure

i. Prepare an autosampler vial containing the DFTPP solution.

ii. Place the vial in the GC autosampler and begin the analytical sequence. The injection volume is 2 µL of the DFTPP calibration standard (25 µg/mL).

iii. Evaluate the DFTPP spectrum, determining if the ion abundances meet the criteria in 3. For EPA 625 and SW846-8270, the method for determining the mass spectrum of DFTPP only mentions the fact that background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions.

iv. Current GC/MS data acquisition and reduction software is capable of evaluating DFTPP by the appropriate analytical method.

v. If the criteria are not met, further analysis is prohibited until corrective action has been taken and the problem resolved.

4. Initial Calibration

a. Requirements

i. An initial five-point calibration curve will be analyzed to determine instrument sensitivity and the linearity of response. Once the curve has been verified, analysis can proceed.

ii. The linear calibration range of the instrument must be determined before the analysis of any samples. For general purposes, a range of 10 to 100 ug/ml on-column has been found to be useful.

iii. Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall sensitivity and the mass spectral characteristics of that compound. The initial calibration requires that the system may not be saturated for high response compounds at 160 ng on-column amount for any semivolatile target compounds.

iv. The instrument must be calibrated using the same instrument conditions that are used to analyze the samples.

v. A Second Source Calibration Verification Standard (SECSTD) must be analyzed immediately after each initial calibration curve.

1) The SECSTD is a calibration standard obtained from a different source than was used for the calibration standards.

2) The SECSTD may contain all or a subset of the target analytes analyzed during the initial calibration.

3) The SECSTD should be analyzed at a concentration equivalent to the Continuing Calibration Standard.

4) The calculated concentration of the compounds in the SECSTD may not exceed the theoretical concentration by more than 20%. If this criterion is not met, further analysis is prohibited until corrective action has been taken and the problem resolved. The average can also be used (per method 8000, section 7.7) for most projects. See project instructions if necessary.

b. Procedure

i. Transfer an aliquot of each of the standards and of the SECSTD as specified in the initial calibration sequence into GC autosampler vials

ii. If the internal standard (IS) has not been prepared as part of the standard solutions, add an aliquot to each vial and seal with a crimp top cap. The IS concentration should be 40 µg/mL.

iii. Place the vials in the GC autosampler and begin the analysis of all initial calibration standards.

iv. Evaluation of calibration-See related calculations in the calculation section

1) Relative Response Factor - The relative response factor of each target analyte is assumed to be invariant over the entire calibration range.

a) Calculate the relative response factor (RRF) for each compound.

b) Calculate the average relative response factor for each compound.

c) Calculate the percent relative standard deviation (%RSD).

d) Compare the %RSD value to the Maximum %RSD values in Table 6. The calculated %RSD may not exceed the maximum value for the compounds listed. If this criterion is

not met, the calibration curve is invalid and must be regenerated with new calibration points or analytical standards.

e) Some compounds have minimum average RRF requirements that must also be met. Refer to Table 4.

f) Linearity - If the %RSD of any compound is 15% 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.

g) If the %RSD of any compound is greater than 15%, the analyst may review the results for these analytes to ascertain if the problem is associated with one of the calibration standards. If a single standard is suspect, it may be reanalyzed, or replaced and reanalyzed.

i) Alternatively, the calibration range may be narrowed by replacing one or more of the calibration standards. Note: changes to the upper range could result in the need for additional dilutions. Changes to the lower range will result in a change in the method quantitation limit and could result in an elevation in the method reporting limit.

ii). The initial calibration may still be valid if the mean of the RSD values for all analytes in the calibration is ≤ 15%. All target analytes that exceed 15% must be identified to the client.

h) If the criteria are not met, further analysis is prohibited until corrective action has been taken and the problem resolved.

v. Analyze the SECSTD as described above and follow the criteria listed.

5. Continuing calibration
   a. Requirements
      i. A continuing calibration standard selected from the middle of the initial calibration range will be analyzed at the beginning of each 12-hour analytical sequence and prior to the analysis of any samples.
      ii. The continuing calibration standard level is 45 µg/mL for Method 8270.
      iii. All calibration criteria must be met. The average %D can also be used per method 8000, section 7.7 for most projects. See project instructions if necessary
   b. Procedure
      i. Transfer an aliquot of the standard into a labeled GC autosampler vial.
      ii. Note that the internal standard has already been added during standards preparation at 40ug/ml.
      iii. Place the vial in the GC autosampler and begin the analysis.
      iv. For each analyte, calculate the %Difference using Equation 3 or %Drift using Equation 4
         1) Compare the %Difference value to the Maximum %Difference values in Table 6. The calculated %Difference may not exceed the maximum value for the compounds listed.
         2) Some compounds have minimum average RRF requirements that must also be met. Refer to Table 4.
         3) If the criteria are not met, further analysis is prohibited until corrective action has been taken and the problem resolved.
      v. For SW-846 8270, compare the extracted ion current profile (EICP) area and retention time (RT) of the IS with those of the mid-point of the initial calibration curve.
         1) When the RT for any internal standard has changed by >30 sec., inspect for malfunctions at the instrument. If malfunctions are determined, make the necessary corrections.
         2) When the EICP area has changed by a factor (-50% to +100%) from the mid-point, inspect the system for malfunctions. If malfunctions are determined, corrections are made as appropriate.

6. Sample analysis
   a. Requirements
      i. A valid initial calibration curve must be available.
      ii. DFTPP and continuing calibration standards must have been analyzed and pass criteria before sample analysis can proceed.
      iii. All analyses must have started within 12 hours after the injection of the valid DFTPP analysis.
      iv. An LCS should be analyzed within the same 12 hour sequence as the MS/MSD. The LCS must have been prepared in the same extraction batch as the MS/MSD. However, under certain circumstances re-analysis occurs in a different 12hour window, but every effort is made to re-analyze on the same instrument at minimum.

v. The method blank associated to any sample preparation batch should be analyzed on all instruments in which any associated sample is analyzed. However, time constraints usually prevent the same method blank from being re-analyzed numerous times. Any method blank or solvent blank can be analyzed to determine that the GC/MS is contamination free.

b. Procedure

i. Prep laboratory technicians store the extracts in the Semi-volatile refrigerator D upon completion.

ii. Internal standard should already be added at this point at 40 µg/ml by the preparation laboratory. In the event it was omitted, add 10 µL of internal standard to each 500ul portion to achieve a 40ug/ml concentration (500ul stock internal standard is reserved for re-analysis/dilutions. It is located in the standards refrigerator in the semi-volatiles area.)

iii. Place the vials in the GC autosampler and type the sequence to begin the analysis.

iv. Sample concentrations are calculated using a different combination of calculations for soil and water samples. Refer to the calculation section.

1) All target analytes must be within the linear calibration range established for the instrument. If a target analyte exceeds the linear calibration range, the sample must be diluted with Methylene chloride. Internal standard is added to equal 40 µg/ml in the extract.

2) All target compounds found in any sample must meet the qualitative criteria in Section 8, "Qualitative Analysis".

3) If required, a search of non-target tentatively identified compounds (TICs) will be made. Review Section 8, "Qualitative Analysis" for additional guidance regarding TICs.

v. Calculate surrogate recoveries.

1) Failing to meet this criterion without justifiable and documented reasons require re-extraction and re-analysis of all affected samples.

- Check to ensure that there are no errors in calculations, formulation of the surrogate compound spiking solutions, and internal standards. Also, check instrument performance. Additionally, verify proper software algorithms and proper integration of peak area.
- Reanalyze the sample if none of the above steps reveal a problem.
- If an undiluted analysis with acceptable surrogate compound recoveries is being submitted, do not submit re-analyzed diluted samples if the surrogate compound recoveries are outside the limits.
- It is not necessary to reanalyze the matrix spike or matrix spike duplicate (MS/MSD), even if the surrogate compound recoveries are outside the limits.
- If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications, it should be reanalyzed only if the MS/MSD surrogate compound recoveries are within the limits. If the sample and associated MS/MSD show the same pattern (i.e., outside the limits), then the sample does not require re-analysis. (The unacceptable surrogate limits are confirmed with the MS/SD analysis showing the same trend.) Document in the narrative the similarity in recoveries of the surrogate compounds in the sample and associated MS/MSD.

2) If the reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, submit only data from the analysis with surrogate compound recoveries within the limits. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

3) If the reanalysis of the sample does not solve the problem (i.e., the surrogate compound recoveries are outside the limits for both analyses), then submit the data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables. Refer to Section 7 where the reanalysis of samples is discussed.

vi. MS/MSD (or LCS/LCSD) calculations

1) Calculate the recovery of each analyte spiked into the MS and MSD (or LCS's) using Equation 9. The spike concentration is normally 40 µg/mL for base neutrals, but extraction records must be verified to confirm this. In the case of LCS's, the native concentration is zero because the analytes were spiked into a blank.

2) Calculate the relative percent difference (RPD) for each target analyte between the two spiked samples using Equation 10.

3) The MS/MSD recovery must be within the laboratory generated or project specific limits for SW-846 8270 and EPA 625.

4) LCS recoveries must be within the laboratory generated or project specific limits for the laboratory.
5) Failing to meet this criterion without justifiable and documented reasons require re-extraction and reanalysis of all affected samples.

7. Re-analysis of Samples
   a. In analytical chemistry, re-analysis of samples is often the rule rather than the exception. In order to uniquely identify reanalyzed sample results, all sample results that are generated from a reanalysis will be identified as such by using suffixes.
   b. The original analysis of any sample, or the most concentrated native sample will not have a suffix.
   c. All subsequent reanalysis of any given sample will be given a suffix, which is added to the end of the Lab Sample ID number. The suffixes are as follows:
      i. DL is used for samples that are reanalyzed at a dilution higher than the original. Thus, if sample 200200102 is analyzed at a dilution of 1:10, the Lab Sample ID for the reanalysis is 200200102DL.
      ii. R is used for samples that are re-analyzed at the same dilution as the original analysis. Reasons for this may include poor surrogate recovery during the first analysis, blank contamination, etc. The first analysis of sample 200200102 uses the sample number as the Lab Sample ID. If the analysis of 200200102 had poor surrogate recoveries and must be reanalyzed; the Lab Sample ID of the reanalysis is 200200102R.
      iii. RE is used for samples that are re-extracted and reanalyzed. The first analysis of sample 200200102 uses the sample number as the Lab Sample ID. If the analysis of 200200102 had poor surrogate recoveries and must be re-extracted and re-analyzed, the Lab Sample ID is 200200102RE.

8. Qualitative Analysis
   a. The Target compounds listed in Table 1 shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. According to PEL Laboratories Inc. Quality Manual, Section 4.5, two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.
      i. For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the same component in the most recent continuing calibration standard. For reference, the standard must be run in the same 12-hour time period as the sample. If samples are analyzed during the same 12-hour time period as the initial calibration standards, use the RRT values from the calibration point with the concentration equal to the daily or continuing standard. The RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.
      ii. For comparison of standard and sample component mass spectra, the mass spectra of each should be obtained on the same GC/MS. Once obtained, these standard spectra may be used for identification purposes, only if the GC/MS meets the daily instrument performance requirements for DFTPP. These standard spectra may be obtained from the run used to obtain reference RRTs.
      iii. The requirements for qualitative verification by comparison of mass spectra are as follows:
         1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
         2) The relative intensities of ions specified in the preceding paragraph must agree within ± 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent).
         3) Ions greater than 10% in the sample spectrum, but not present in the standard spectrum, must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra.
      iv. If a compound cannot be verified by all of the above criteria, but in the technical judgement of the analyst and reviewer, the identification is correct, then the analyst shall report that identification and proceed with quantification.

b. Internal standard responses and retention times in all standards, blanks, samples, and QC samples, must be evaluated immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (or 12-hour) calibration standard, then the chromatographic system must be inspected for malfunctions. Any malfunctions found must be corrected and any samples analyzed during the same time period should be re-analyzed. Compare the internal standard responses and retention times against the mid-point calibration standard or average RRF, depending on the analytical method. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, LCS, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples while the system was malfunctioning is necessary.
   i. If after re-analysis, the EICP areas for internal standards are inside the acceptance limits (-50% to +100%), and then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, submit only data from the analysis with EICPs within the acceptance limits. This is considered the initial analysis and must be reported as such on all data deliverables.
   ii. If the re-analysis of the sample does not solve the problem, (i.e., the EICP areas are outside the contract limits for both analyses), then submit the EICP data and sample data from both analyses. Changes in EICP areas possibly due to matrix interferences. Distinguish between the initial analysis and the reanalysis on all data deliverables. Document in the case narrative all inspection and corrective actions taken.

c. A library search shall be executed for non-target sample components for the purpose of tentative identification. For this purpose, the most recent available release of the NIST/EPA/MSDC mass spectral library shall be used. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.
   i. Up to 20 organic compounds of greatest apparent concentration not in the client specific target analyte list, excluding the system monitoring compounds, shall be tentatively identified via a forward search of the NIST/EPA/MSDC Library. Substances with responses less than 10% of the nearest internal standard are not required to be searched in this fashion. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral analyst assign a tentative identification.
   ii. Guidelines for making tentative identification:
      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.
      2) The relative intensities of the major ions should agree within ± 20% (Example: For an ion with an abundance of 50 percent of the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)
      3) Molecular ions present in reference spectrum should be present in sample spectrum.
      4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
      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 co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.
   iii. If, in the technical judgment of the GC/MS analyst, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral analyst should give additional classifications of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

9. Quantitative Analysis
   a. For level 3 and 4 projects, when target compounds are above the MDL, but below the reporting limit and the spectra meet the identification criteria the concentration is reported with the appropriate qualifier.
   b. An estimated concentration for non-target components tentatively identified shall be determined by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard.

i. A relative response factor (RRF) of one (1) is to be assumed.
ii. The resulting concentration is qualified as "J" (estimated, due to lack of a compound-specific response factor), and "N" (presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target component. The Target software is automatically set up to code non-target analytes as such.

c. If the on-column concentration of any compound in any sample exceeds the initial calibration range, a new aliquot of that sample must be diluted and re-injected. Guidance in performing dilutions and exceptions to this requirement are given below.
i. Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.
ii. The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.
iii. Try not to submit data for more than two analyses. For example report the original sample and one dilution or, if the semi-volatile screening procedure was employed, submit the most concentrated dilution analyzed and one further dilution.

CALCULATIONS

$$RRF = \frac{\text{Area of target analyte}}{\text{Area of internal standard}} \times \frac{\text{Concentration } (\mu g/mL) \text{ of internal standard}}{\text{Concentration } (\mu g/mL) \text{ of target analyte}}$$

Equation 1. Calculation of relative response factors (RRF).

$$\%RSD = \frac{\text{Standard deviation from RRF distribution}}{\overline{RRF}} \times 100$$

Equation 2. Calculation of %RSD.

$$\%Diff = \frac{RRF - \overline{RRF}}{\overline{RRF}} \times 100$$

Equation 3. Calculation of %Difference for continuing calibration standards.

$$\%Drift = \frac{\text{Raw conc. } (\mu g/mL) \text{ found} - \text{Raw conc. } (\mu g/mL) \text{ theoretical}}{\text{Raw conc. } (\mu g/mL) \text{ theoretical}} \times 100$$

Equation 4. Calculation of %Drift for continuing calibration standards.

$$\text{Raw conc. } (\mu g/mL) = \frac{\text{Response - Intercept}}{\text{Slope}} = \left(\frac{\text{Area of target compound}}{\text{Area of internal standard}}\right) x \left(\frac{\text{Concentration of internal standard } (\mu g/mL)}{\overline{RRF} \text{ or } RRF_{\text{Daily standard}}}\right)$$

Equation 5. Calculation of raw concentration.

$$\text{Sample concentration } (\mu g/L) = \left(\frac{\text{Raw conc. } (\mu g/mL) \text{ x Dil. factor x Final extract volume (mL)}}{\text{Sample amount (L)}}\right)$$

Equation 6. Calculation of concentration in water samples.

$$\text{Sample concentration } (\mu g/Kg) = \left(\frac{\text{Raw conc. } (\mu g/mL) \text{ x Dil. factor x Final extract vol. (mL)}}{\text{Weight of sample analyzed (Kg) x } \%Solids/100}\right)$$

Equation 7. Calculation of target analyte concentration in soils.

$$\text{Surrogate recovery (\%)} = \frac{\text{Raw conc. found } (\mu g/mL) \times \text{Dil. factor}}{\text{Conc. spiked } (\mu g/mL)} \times 100$$

Equation 8. Calculation of surrogate recovery.

$$\%R = \frac{\text{Conc. found in spike } (\mu g/L \text{ or } \mu g/Kg) - \text{Conc. found in native sample } (\mu g/L \text{ or } \mu g/Kg)}{\text{Conc. spiked } (\mu g/L \text{ or } \mu g/Kg)} \times 100$$

Where:

$$\text{Conc. spiked} = \frac{\text{Spiking standard concentration } (\mu g/mL) \times \text{Volume spiked (mL)}}{\text{Amount of sample used for matrix spike (L or Kg)}}$$

Equation 9. Calculation of spike recovery.

$$\%RPD = \frac{(\text{Raw amount found in the MS} - \text{Raw amount found in the MSD})}{(\text{Raw amount found in the MS} + \text{Raw amount found in the MSD})} \times 200$$

Equation 10. Calculation of relative percent difference between duplicate matrix spikes.

DOCUMENTATION

Documentation must follow the requirements of PEL Laboratories, Inc Quality Manual and the Rules for Documentation SOP.

All analyses will be documented in a logbook. Each logbook will be uniquely identified with the instrument identification name(example SVMSD03) and dates used. Each page within the bound logbooks will have a unique page number. Each analytical sequence should be logged into the log book (follow the instrument log-book SOP) and include the following for each sequence:

1. The name of the instrument method and method number if not included in the method name.
2. For each analysis made, the analyst must: (Refer to Data Analysis SOP for further information)
   a. Include a sample description.
      i. For samples, this is the Lab Sample ID, including any suffixes as may apply.
      ii. For standards, the analyst should indicate the concentration of the standard followed by CCV and the number of the CCV in the sequence (i.e.45ccv1 is the first standard analyzed for a particular sequence 45ccv4 would be the fourth ccv analyzed in a sequence). Additionally, in the sample field section, the unique SV number of the mid-level standard is included for tracking purposes. An example is SV907bset.
      iii. For blanks, the analyst should use the extraction date followed by the letters BLK and the letter of the matrix. For example, a soil blank extracted on 11/30/99 could be 113099BLKS. If there is more than soil extracted on that day it would be 113099BLKS1, 113099BLKS2 and so on to distinguish. This applies equally to all blanks, regardless of whether they are system or method blanks.
   b. Include sample prep batch.
   c. Use correct sub-list.
   d. Use proper sample type.
   e. If data is not to be used for reporting, then append an "X" to the end of the sample ID.
3. Backups are conducted weekly for Target data onto CD and are stored for future retrieval.

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

- US EPA Contract Laboratory Program Statement of Work, CLP OLM 1.9
- 40 CFR Part 136. Appendices A-D, Method 625
- *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 8270
- PEL Laboratories, Inc Quality Manual; Revision 2; 12/2/99

Table 1. Analyte cross-reference table.

Semivolatile Compounds	CAS Number	625/8270 Standard	8270/ App IX
Acenaphthene	83-32-9	•	•
Acenaphthylene	208-96-8	•	•
Aniline	62-53-3	•	•
Anthracene	120-12-7	•	•
Benzidine	92-97-5	•	•
Benzo(a)anthracene	56-55-3	•	•
Benzo(a)pyrene	50-32-8	•	•
Benzo(b)fluoranthene	205-99-2	•	•
Benzo(g,h,i)perylene	191-24-2	•	•
Benzo(k)fluoranthene	207-08-9	•	•
Benzyl alcohol	100-51-6	•	•
bis(2-Chloroethoxy) methane	111-91-1	•	•
bis(2-Chloroethyl) ether	111-44-4	•	•
bis(2-Chloroisopropyl)ether or 2,2'-oxybis (1-Chloropropane)	108-60-1	•	•
bis(2-Ethylhexyl) phthalate	117-81-7	•	•
4-Bromophenyl-phenylether	101-55-3	•	•
Butylbenzylphthalate	85-68-7	•	•
4-Chloroaniline	106-47-8	•	•
4-Chloro-3-methylphenol	59-50-7	•	•
2-Chloronaphthalene	91-58-7	•	•
2-Chlorophenol	95-57-8	•	•
4-Chlorophenyl-phenylether	7005-72-3	•	•
Chrysene	218-01-9	•	•
Dibenz(a,h)anthracene	53-70-3	•	•
Dibenzofuran	132-64-9	•	•
1,2-Dichlorobenzene	95-50-1	•	•
1,3-Dichlorobenzene	541-73-1	•	•
1,4-Dichlorobenzene	106-46-7	•	•
3,3-Dichlorobenzidine	91-94-1	•	•
2,4-Dichlorophenol	120-93-2	•	•
Diethylphthalate	84-66-2	•	•
Dimethylphthalate	131-11-3	•	•
2,4-Dimethylphenol	105-67-9	•	•
Di-n-butylphthalate	84-74-2	•	•
Di-n-octylphthalate	117-84-0	•	•
4,6-Dinitro-2-methylphenol	534-52-1	•	•
2,4-Dinitrophenol	51-28-5	•	•
2,4-Dinitrotoluene	121-14-2	•	•
2,6-Dinitrotoluene	606-20-2	•	•
Fluoranthene	206-44-0	•	•
Fluorene	86-73-7	•	•
Hexachlorobenzene	118-74-1	•	•
Hexachlorobutadiene	87-68-3	•	•
Hexachlorocyclopentadiene	77-47-4	•	•
Hexachloroethane	67-72-1	•	•
Indeno(1,2,3-cd)pyrene	193-39-5	•	•
Isophrone	78-59-1	•	•

Semivolatile Compounds	CAS Number	625/8270 Standard	8270/ App IX
1-Methylnaphthalene	90-12-0	•	•
2-Methylnaphthalene	91-57-6	•	•
2-Methylphenol	95-48-7	•	•
3 and 4-Methylphenol	106-44-5	•	•
N-Nitroso-di-n-propylamine	621-64-7	•	•
N-Nitrosodiphenylamine	86-30-6	•	•
Naphthalene	91-20-3	•	•
2-Nitroaniline	88-74-4	•	•
3-Nitroaniline	99-09-2	•	•
4-Nitroaniline	100-01-6	•	•
Nitrobenzene	98-95-3	•	•
2-Nitrophenol	88-75-5	•	•
4-Nitrophenol	100-02-7	•	•
Pentachlorophenol	87-86-5	•	•
Phenanthrene	85-01-8	•	•
Phenol	108-95-2	•	•
Pyrene	129-00-0	•	•
1,2,4-Trichlorobenzene	120-82-1	•	•
2,4,5-Trichlorophenol	95-95-4	•	•
2,4,6-Trichlorophenol	88-06-2	•	•
Acetophenone	98-86-2		•
2-Acetylaminofluorene	53-96-3		•
4-Aminobiphenyl	92-67-1		•
Aramite	140-57-8		•
Carbazole	86-74-8		•
2,6-Dichlorophenol	87-65-0		•
p-Dimethylaminoazobenzene	60-11-7		•
3,3'-Dimethylbenzidine	119-93-7		•
7,12-Dimethylbenz(a)anthracene	57-97-6		•
1,3-Dinitrobenzene	99-65-0		•
1,2-Diphenylhydrazine (Azobenzene)	122-66-7		•
Diallate	2303-16-4		•
Ethyl methanesulfonate	62-50-0		•
Hexachloropropene	1888-71-7		•
Isodrin	465-73-6		•
Isosafrole	120-58-1		•
Methapyriline	91-80-5		•
Methyl methanesulfonate	66-27-3		•
3-Methylcholanthrene	56-49-5		•
3-Methylphenol	108-39-4		•
N-Nitroso-di-n-butylamine	924-16-3		•
N-Nitrosodiethylamine	55-18-5		•
N-Nitrosodimethylamine	62-75-9		•
N-Nitrosomethylethylamine	10595-95-6		•
N-Nitrosomorpholine	59-89-2		•
N-Nitrosopiperidine	100-75-4		•
N-Nitrosopyrrolidine	930-55-2		•
1,4-Naphthoquinone	130-15-4		•
1-Naphthylamine	134-32-7		•
2-Naphthylamine	91-59-8		•

Semivolatile Compounds	CAS Number	625/8270 Standard	8270/ App IX
5-Nitro-o-toluidine	99–55–8		•
4-Nitroquinoline-1-oxide	56–57–5		•
Pentachlorobenzene	608–93–5		•
Pentachloronitrobenzene	82–68–8		•
Phenacetin	62–44–2		•
Phenyl-tert-butylamine	122–09–8		•
1,4-Phenylenediamine	106–50–3		•
2-Picoline	109-06-8		•
Pronamide	23950-58-5		•
Pyridine[a]	110-86-1	•	•
Safrole	94–59–7		•
1,2,4,5-Tetrachlorobenzene	95-94-3		•
2,3,4,6-Tetrachlorophenol	58-90-2		•
o-Toluidine	95–53–4		•
1,3,5-Trinitrobenzene	99-35-4		•
Dibenz (a,j) acridine[b]	224-42-0		
3,4-Dichlorophenol[b]	95-77-2		

[a]Pyridine is standard for TCLP analysis or special request only
[b]Additional analytes that may be requested for analysis that are not typical for standard or APPIX lists.

Table 2. Characteristic Ions for Semivolatile Target Compounds, Surrogate Compounds and Internal Standards.

Semivolatile Compounds	Primary Ion[a]	Secondary Ion(s)
Acenaphthene	154	153, 152
Acenaphthylene	152	151, 153
Aniline	93	66, 65
Anthracene	178	176, 179
Benzidine	184	92, 185
Benzoic Acid	122	105, 77
Benzo(a)anthracene	228	229, 226
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(g,h,i)perylene	276	138, 277
Benzo(a)pyrene	252	253, 125
Benzyl Alcohol	108	79, 77
bis(2-Chloroethyl) ether	93	63, 95
bis(2-Ethylhexyl) phthalate	149	167, 279
4-Bromophenyl phenyl ether	248	250, 141
Butyl benzyl phthalate	149	91, 206
4-Chloroaniline	127	129
2-Chloronaphthalene	162	127, 164
4-Chloro-3-methylphenol	107	144, 142
2-Chlorophenol	128	64, 130
4-Chlorophenyl phenyl ether	204	206, 141
Chrysene	228	226, 229
Dibenz(a,h)anthracene	278	139, 279
Dibenzofuran	168	139
Di-n-butyl phthalate	149	150, 104
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
1,2-Dichlorobenzene	146	148, 111

Semivolatile Compounds	Primary Ion[a]	Secondary Ion(s)
3,3'-Dichlorobenzidine	252	254, 126
2,4-Dichlorophenol	162	164, 98
Diethyl phthalate	149	177, 150
2,4-Dimethylphenol	122	107, 121
Dimethyl phthalate	163	194, 164
4,6-Dinitro-2-methylphenol	198	51, 105
2,4-Dinitrophenol	184	63, 154
2,4-Dinitrotoluene	165	63, 89
2,6-Dinitrotoluene	165	63, 89
Di-n-octyl phthalate	149	167, 43
Fluoranthene	202	101, 203
Fluorene	166	165, 167
Hexachlorobenzene	284	142, 249
Hexachlorobutadiene	225	223, 227
Hexachlorocyclopentadiene	237	235, 272
Hexachloroethane	117	201, 199
Indeno(1,2,3-cd)pyrene	276	198, 227
Isophorone	82	95, 138
1-Methylnaphthalene	142	141
2-Methylnaphthalene	142	141
2-Methylphenol (o-Cresol)	108	107, 79
3 and 4-Methylphenol (m and p-Cresol)	108	107, 79
Naphthalene	128	129, 127
2-Nitroaniline	65	92, 138
3-Nitroaniline	138	108, 92
4-Nitroaniline	138	108, 92
Nitrobenzene	77	123, 65
2-Nitrophenol	139	109, 65
4-Nitrophenol	139	109, 65
N-Nitrosodimethylamine	42	74, 44
N-Nitrosodiphenylamine	169	168, 167
N-Nitrosodipropylamine	70	42, 101, 130
2,2'-oxybis-(1-Chloropropane)	45	77,121
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Phenol	94	65, 66
2-Picoline	93	66, 92
Pronamide	173	175, 145
Pyrene	202	200,203
Pyridine	79	52
1,2,4-Trichlorobenzene	180	182, 145
2,4,5-Trichlorophenol	196	198, 200
2,4,6-Trichlorophenol	196	198, 200

System Monitoring Compounds		
Compound	**Primary Ion[a]**	**Secondary Ion**
2-Fluorobiphenyl	172	171
2-Fluorophenol	112	64
Nitrobenzene-d5	82	128, 54
Phenol-d5	99	42,71
Terphenyl-d14	244	122, 212
2,4,6-Tribromophenol	330	332, 141
Internal Standards		
Compound	**Primary Ion**	**Secondary Ion**
1,4-Dichlorobenzene-d4	152	115
Naphthalene-d8	136	68
Acenaphthene-d10	152	115
Phenanthrene-d10	136	68
Chrysene-d12	164	162, 160
Perylene-d12	188	94, 80

[a]The primary ion should be used unless interferences are present, in which case, a secondary ion may be used.

Table 3.DFTPP Ion Abundance Criteria for 625 and 8270

Mass	Ion Abundance Criteria
51	30.0 to 60.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	40.0 to 60.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance
199	5.0 to 9.0 percent of mass 198
275	10.0 to 30.0 percent of mass 198
365	Greater than 1.0 percent of mass 198
441	Present but less than mass 443
442	greater than 40 percent of mass 198
443	17.0 to 23.0 percent of mass 198

Table 4. SW-846 8270 Relative Response Factor Criteria For Initial and Continuing Calibration of Semivolatile Organic Compounds.

Calibration Check Compounds (CCC) [a]			
Semivolatile Compounds	**Minimum RRF**	**Maximum % RSD**	**Maximum % Difference**
Acenaphthene	----	30	20
1,4-Dichlorobenzene	----	30	20
Hexachlorobutadiene	----	30	20
N-Nitrosodiphenylamine	----	30	20
Di-n-octyl phthalate	----	30	20
Fluoranthene	----	30	20
Benzo(a)pyrene	----	30	20
4-Chloro-3-methylphenol	----	30	20
2,4-Dichlorophenol	----	30	20
2-Nitrophenol	----	30	20
Phenol	----	30	20
Pentachlorophenol	----	30	20
2,4,6-Trichlorophenol	----	30	20

System Performance Check Compounds (SPCC)[b]			
Semivolatile Compounds	**Minimum RRF**	**Maximum % RSD**	**Maximum % Difference**
N-Nitroso-di-n-propylamine	0.050	15	20
Hexachlorocyclopentadiene	0.050	15	20
2,4-Dinitrophenol	0.050	15	20
4-Nitrophenol	0.050	15	20

[a] Most of the CCCs are expected to meet the less than 15%RSD required of the other target analytes. PEL Laboratories, Inc makes every attempt for all parameters to meet the 15%RSD and the 30%RSD is only used as necessary.

[b] These compounds typically have RRFs of 0.1 to 0.2 and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate.

Table 5. Required Mass Spectrometer Analytical Conditions.

Electron Energy	70 volts (nominal)
Mass Range	35-500 amu
Scan Time	To give at least 5 scans per peak, not to exceed 1 second per scan for capillary column
Transfer Line Temperature	270°C
Source Temperature	180°C

Table 6. Semivolatile Internal Standards With Corresponding Target Compounds and System Monitoring Compounds Assigned For Quantitation.

1,4-Dichlorobenzene-d_4	**Naphthalene-d_8**	**Acenaphthene-d_{10}**
Aniline	----	Acenaphthene
Benzyl alcohol	Benzoic Acid	Acenaphthylene
2,2'-oxybis-(1-Chloropropane)	bis(2-Chloroethoxy)methane	2-Chloronaphthalene
bis(2-Chloroethyl) ether	4-Chloroaniline	4-Chlorophenyl-phenyl ether
2-Chlorophenol	4-Chloro-3-methylphenol	Dibenzofuran
1,3-Dichlorobenzene	2,4-Dichlorophenol	Diethyl phthalate
1,4-Dichlorobenzene	2,6-Dichlorophenol	Dimethyl phthalate
1,2-Dichlorobenzene	----	2,4-Dinitrophenol
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrotoluene
Hexachloroethane	Hexachlorobutadiene	2,6-Dinitrotoluene
Methyl methanesulfonate	Isophorone	Fluorene
2-Methylphenol	1-Methylnaphthalene	2-Fluorobiphenyl (surrogate)
4-Methylphenol	2-Methylnaphthalene	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	Naphthalene	1-Naphthylamine
N-Nitroso-di-n-propylamine	Nitrobenzene	2-Naphthylamine
Hexachloroethane	Nitrobenzene-d8 (surrogate)	2-Nitroaniline
Phenol	2-Nitrophenol	3-Nitroaniline
2-Fluorophenol (surrogate)	N-Nitroso-di-n-butylamine	4-Nitroaniline
Phenol-d5 (surrogate)	N-Nitrosopiperidine	4-Nitrophenol
2-Picoline	1,2,4-Trichlorobenzene	Pentachlorobenzene
Pyridine	1,2,4,5-Tetrachlorobenzene	Phenacetin
Acetophenone	----	2,3,4,6-Tetrachlorophenol
----	----	2,4,6-Tribromophenol (surr.)
----	----	2,4,6-Trichlorophenol
----	----	2,4,5-Trichlorophenol
----	----	

Phenanthrene-d10	Chrysene-d12	Perylene-d12
4-Aminobiphenyl	Benzo(a)anthracene	Benzo(b)fluoranthene
Anthracene	bis(2-Ethylhexyl) phthalate	Benzo(k)fluoranthene
4-Bromophenyl-phenyl ether	Butylbenzyl phthalate	Benzo(g,h,i)perylene
Benzidine	Chrysene	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	3,3'-Dichlorobenzidine	Indeno(1,2,3-cd)pyrene
Phenanthrene	p-Dimethylamino-azobenzene	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	Pyrene	7,12-Dimethyl-benzo(a)anthracene
Fluoranthene	Terphenyl-d14 (surrogate)	Di-n-octyl phthalate
Hexachlorobenzene	----	3-Methylcholanthrene
N-Nitrosodiphenylamine	----	----
Pentachlorophenol	----	----
Pentachloronitrobenzene	----	----
Pronamide	----	----
----	----	----
----		----

Appendix A

Variations to this SOP for AFCEE 3.0 Analysis

Since the AFCEE QAPP 3.0 is very specific, all information available in the QAPP will not be repeated in this SOP. Anyone dealing with AFCEE should have a copy of the QAPP and be familiar with its contents.

1. Extraction
   a) Holding times will be met according to the time of sample collection (with correction for time zone differences).
   b) Sample extraction time will be recorded in addition to extraction date. (This is the time extraction is started)

2. Calibration
   a) Initial calibration criteria listed in this SOP is valid. Three additional options are also provided in the AFCEE QAPP , but PEL Laboratories only utilizes the following two:
      i) Curve must have mean ≤ 15% RSD for all analytes. With no single analyte >30%.
      ii) Linear – least squared regression, r > 0.995
   b) Second vendor standards must be ≤ 25% difference. (We normally follow CCV criteria of ≤ 20% difference)
   c) Lowest point of initial calibration must be at or below AFCEE report limits.
   d) SPCCs can be averaged ≥0.050
   e) All calibration analytes must be within +/- 20% of expected value-no averaging permitted.
   f) Internal standard requires retention time +/- 30 seconds from retention time of the mid-point on the initial calibration. (The software currently references from our last CCV utilized.)

3. Surrogates
   a) Acceptability is not based on laboratory established limits.
   b) Acceptance limits for waters and soils are listed in AFCEE QAPP.

4. Spikes
   a) Multiple reagent spikes (LCS, MS, MSD) will be prepared depending on requested target list.
   b) Matrix spike and matrix spike duplicates (MS/MSD) will be prepared as requested by project.
   c) Acceptability is not based on laboratory established limits.
   d) Quality Control Acceptance limits for waters and soils are listed in AFCEE QAPP.
   e) Because the MS/MSD are included in the batch, only 18 field samples may be analyzed in an AFCEE batch.

5. Data Reduction/Reporting
   a) AFCEE reporting limits are listed in the AFCEE QAPP and are different from PEL Laboratories standard reporting limits.
   b) MDL must be less than one-half of AFCEE reporting limit.
   c) Data are qualified to the MDL based on instructions in AFCEE QAPP.
   d) Significant figure rules do not apply. AFCEE requires that MDLs and results are reported to one more decimal place than AFCEE reporting limit, without regard to significant digits.
   e) MDLs and report limits are not corrected for dry weight or dilution on the Form O-2, however initial weights extracted are raised based on percent solids.
   f) Qualifiers are applied to results based on instructions in AFCEE QAPP.
   g) AFCEE deliverables are designated in AFCEE QAPP.

6. Corrective action is identified in the AFCEE QAPP

Appendix B: STANDARDS PREPARATION

Regular 625/8270 primary standards preparation:

Analyte/mix	Vendor	Catalog #	Conc. in ug/ml
Pyridine	Supelco	4-8305	2000
1-M-Nap	Accustd	S-518A	2000
Acid Surr.	Ultra	ISM-295	2000
B/N Mix #1	Ultra	US-100	2000
B/N Mix #2	Ultra	US-101	2000
Phenol Mix	Ultra	US-107	2000
Pah Mix	Restek	31011	2000
Tox Mix #1	Ultra	US-103	2000
Tox Mix #2	Ultra	US-104	2000
Benzidine Mix	Ultra	US-105	2000
Carbazole	Supelco	4-8076	2000
Custom 3	NSI	Q-2572	2000
B/N Surr.	Ultra	ISM-285	1000
3,4-Dichlorophenol	Accustd		1000

An 8270 "top" intermediate is prepared using 500ul of B/N surrogate at 1000ug/mL, 500ul of 3,4-dichloropenol at 1000ug/ml, and 250ul of the other 12 mixes at 2000ug/mL. The final volume is 5mLs with DCM as the diluent.
6 levels are prepared from the top std ranging from 10-100ug/ml

100 std		1mL w/DCM + 20ul of 625/8270 internal standard
75 std	750ul top	Dilute to 1mL w/DCM + 20ul of 625/8270 internal standard
60 std	600ul top	Dilute to 1mL w/DCM + 20ul of 625/8270 internal standard
45 std	450ul top	Dilute to 1mL w/DCM + 20ul of 625/8270 internal standard
20 std	200ul top	Dilute to 1mL w/DCM + 20ul of 625/8270 internal standard
10 std	100ul top	Dilute to 1mL w/DCM + 20ul of 625/8270 internal standard

Regular 625/8270 secondary standards preparation:

Analyte/mix	Vendor	Catalog #	Conc. in ug/ml
BNA Custom Mix	NSI	Q-1173	150

45 std	300ul mix	Dilute to 1mL w/DCM + 20ul of 625/8270 internal standard.

(DCM=Dichloromethane)

Sample Analysis: TOC
Method 415.1/9060 (total organic carbon, liquid and solid)

APPROVED:

Sample Prep. Section Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. for the determination of TOC in drinking, surface, and saline waters, domestic and industrial wastes, and soils.

This method is most applicable to measurement of TOC above 1 mg/L.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

Interferences

Carbonate and bicarbonate carbon represent interference under the terms of this test and must either be removed or accounted for in the final calculation.

This method is applicable to homogenous samples that can be injected into the apparatus by means of a microliter syringe. The syringe openings limit the size of particles that may be included in the sample.

Method Summary

Organic carbon is measured using a carbonaceous analyzer. This converts the organic carbon in a sample to carbon dioxide by catalytic combustion. The CO_2 which is formed is then measured directly by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in a sample.

QA/QC REQUIREMENTS

The holding time for this test is 28 days from the time of sampling.

This SOP was written to conform to all QA/QC criteria described in the following methods: EPA 415.1 / 9060.

The following control samples should be run with each batch of samples. A batch is defined as 20 field samples, or 18 field samples **for AFCEE**:

1. Method Blank: An analyte free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. Used to check for any contamination within the analytical system.
2. Initial Calibration Verification (ICV): A secondary source matrix spike used to verify the calibration curve. True value is given and percent recovery is calculated. The recovery on the ICV must be within +/- 20% of the true value for acceptance. Each analysis batch must begin with an ICV and be followed by a Continuing Calibration Verification (CCV) sample at the end of the batch. In addition, a CCV is run every ten samples to verify the stability of the system.

3. Initial Calibration Blank (ICB): An analyte free matrix that is the same as the carrier for the test. A sample blank is run immediately following the ICV to check for contamination within the system. In addition, a Continuing Calibration Verification (CCB) is run at the end of the batch as well as every ten samples to check for contamination within the system and carryover from sample to sample.

4. Laboratory Control Sample (LCS): Sample of known matrix, spiked with analytes and carried through the preparation and analysis procedure as a sample. The ICV/ICB is followed by a Laboratory Control Sample, the true value is given and the percent recovery is calculated. The recovery of the LCS sample must be within 80 – 120%. When the recovery is outside of this range, the system must be checked, a new LCS sample made up, and the associated blank and batch of samples are re-analyzed. Any out of control event that references client data must be documented in the case narrative (Level II, III, and IV packages) and/or a corrective action report (CAR) form.

5. Matrix Spikes (MS) and Matrix Spike Duplicates (MSD): Matrix Spikes and Matrix Spike Duplicates are aliquots of sample spiked with a known concentration of target analytes. MS and MSD are run every batch. The MS and MSD must have a percent recovery between 75 – 125%, of the sample plus the known spike concentration. In addition, the RPD between the MS and MSD must be less then 20%.

EQUIPMENT/APPARATUS

1. Shimadzu TOC 5050A (liquids)
   a. Automatic sampler
2. Shimadzu Solid Sample Module (SSM-5000A)
3. Test tubes for liquid samples
4. Weigh boats for solid samples

REAGENTS

1. Deionized Water (ASTM Type II Reagent Water).
2. Hydrochloric acid
3. Potassium Hydrogen Phthalate
4. Sodium Carbonate
5. Sodium Benzoate
6. Phosphoric acid 25 %
7. Carbon standards, organic (liquid). One for the ICV/CCV and the other for the TC calibration curve, LCS, and MS/MSD. 1.00 mL = 1.00 mg Organic Carbon (1000 ppm)
8. Carbon standard, inorganic (liquid); for the IC calibration curve. 1.00 mL = 1.00 mg Inorganic Carbon (1000 ppm)

PROCEDURE

1. Liquid Samples:
   a. Turn power on
   b. Go to #6 on the main menu, to monitor the baseline.
   c. Turn on gas, if not already open.
   d. Turn on furnace; allow it to heat up to 680°C.
   e. Once a stable baseline has been obtained, go to #9 of the main menu.
   f. Select the number of samples to analyze and press enter.

g. Load samples into the test tubes, preceded by the correct QC, and followed with a CCV and CCB every 10 samples

h.Press the start button, and allow the needle to find it's "home position".

i. The TOC machine will automatically print the results of each sample.

2. Solids:

a. Weigh boats will be tared and the weight of each sample is recorded, in the logbook. Weigh 100-300 mg of the sample in the boat.

b. One sample is weighed for TC ICV/CCVs and one for IC ICV/CCVs, as well as the other QC samples.

c. The unknown samples will need eight weigh boats apiece. Four for TC and /four for IC. Both the average and the range of the results are reported for solid TOC.

d. Just prior to analysis 0.5 mL phosphoric acid is added to the IC weigh boat to be analyzed.

e. Turn on Shimadzu 5050A and go the main menu.

f. Select SSM for the sample type from the ASI initial menu, and press enter.

g. Turn on gas and furnace.

h. Go to #2 on the main menu to begin analyzing samples.

i. Follow the on-screen prompts for sample analysis.

j. After each TC or IC is analyzed hit F1 (NEXT) to print the graph.

3. Preparation of Calibration Curve:

a. The calibration curve is prepared first for TC, using three points and a blank. Then a separate calibration curve is prepared for IC, using again three points and a blank.

b. The calibration curve fit type, is 1st order Polynomial.

c. The correlation coefficient must be ≥ 0.995.

4. FIGURE 2, shows a sample run and the necessary QC as well as the necessary recovery for each.

FIGURE 2

Sample Number	Sample	Comments
	ICV	80 to 120% Recovery
	ICB	|ICB| < MDL
1	PBA	|PBA| < MDL
2	LCS	80 to 120 % Recovery
3	Sample 1	
4	Sample 2	
5	Sample 3	
6	Sample 4	
7	Sample 5	
8	Sample 6	
9	Sample 6 MS	75 to 125 % Recovery
10	Sample 6 MSD	RPD of < 20%
	CCV	80 to 120 % Recovery
	CCB	|CCB| < MDL

11	Sample 7	
12	Sample 8	
13	Sample 9	
14	Sample 10	
15	Sample 11	
16	Sample 12	
17	Sample 13	
18	Sample 14	
19	Sample 15	
20	Sample 16	
	CCV	80 to 120 % Recovery
	CCB	|CCB| < MDL

CALCULATION

Standard curve is prepared by plotting peak heights of processed standards against known concentrations. Concentration of samples is computed by comparing sample peak heights or peak area with standard curve.

The total amount of organic carbon is calculated by subtracting the total amount of inorganic carbon from the total amount of carbon.

REVIEW/VALIDATION

Data review and validation must be reviewed by the section supervisor according to PEL Laboratories, Inc. Quality Manual. Refer to SOP00085-QA, *Data Review and Verification* for more detailed review procedures. After the data review process has been completed, copies of the data logbook and raw data strips are made from the LIMS environment.

REPORTING

TOC results are reported in units of mg/L for liquid and mg/kg for solids.

All analysis data should be recorded in the Lachat logbook. All pertinent information such as sample size, dilution factors, date(s) of analysis, and sample ID is included. As the analysis proceeds, problems, variations, and other information are written in the logbook immediately.

DOCUMENTATION

Documentation must follow the requirements in PEL Laboratories' Quality Manual and SOP00040-QA; *Rules for Documentation.*

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses are required in the prep building at all times and gloves and lab coats are highly recommended by management. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

POLLUTION AND PREVENTION

Pollution and Prevention encompasses any technique that reduces or eliminates the quantity and/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

For more information about pollution prevention consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477

WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable Federal, state, and local rules and regulations. 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 sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477

REFERENCES

- Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, March 1983. Method 415.1.
- Test Methods for Evaluating Solid Waste, SW-846, Update III, December 1996, Method 9060, GPO #955-001-00000-1.

PEL Laboratory - Standard Operating Procedure

Sample Analysis: Metals by GFAA (Graphite Furnace Atomic Absorption)

APPROVED:

Trace Metals Team Leader Date

Quality Assurance Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. to analyze water samples for metals by graphite furnace atomic absorption spectroscopy. This SOP was written to conform with all quality assurance/quality control (QA/QC) requirements described in SW-846 7000 series methods. The intention of this SOP is to allow individual analysis of samples by the method listed.

The reporting limit for each analyte is specified in each element parameter page of the operating software.

Table 1 lists the analytical sequence that includes calibration standards, field samples, and quality control samples. Figure 1 is a flowchart for analysis of all samples. This flowchart describes the decision making process encountered during a typical furnace analysis procedure.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

QA/QC REQUIREMENTS

1. Initially the following requirements must be met.
   a. MDLs (must be repeated every 12 months) - A minimum of seven samples are prepared at a concentration between 1-10 times the expected MDL. The samples are analyzed within a valid analytical sequence. The validated detection limit is calculated by multiplying the standard deviation of the replicate results by 3.143, which is the one-sided Student's t value for a 99% confidence interval and 6 degrees of freedom. Reporting limits are valid only if they are greater than or equal to the validated method detection limit values. Standard reporting limits can be any convenient value that meets the above criterion. However, the reporting limit for each target must be reconsidered for every sample by reviewing the maximum contaminant level for each element.
   b. Four replicates - Method performance validation is performed by analyzing at least four replicate spiked water samples. To establish initial method precision and accuracy, calculate mean % recovery and percent relative standard deviation (RSD) of each target compound.
2. Holding time for aqueous and non-aqueous samples is 180 days.
3. Calibration curve. No samples may be analyzed until an acceptable calibration curve has been established and verified.
   a. Calibration curve must include a blank and at least 3 standards.
   b. Calibration curve is run daily and must have a correlation coefficient ≥ 0.995.

4. Initial Calibration Verification (ICV). The accuracy of the instrument's calibration must be verified by comparison of the calibration standards to an independent standard (ICV) derived from a second vendor source. Run the ICV (at or near midpoint of curve) after calibration. Criterion is 90-110%. If the ICV fails criterion, re-analyze once. If it still fails, correct problem and recalibrate.

5. Initial Calibration Blank (ICB). The ICB is a reagent blank that must be analyzed after the ICV. The absolute value of the ICB may not exceed the RL. If the ICB fails, re-analyze once. If it still fails, correct problem and recalibrate

6. Continuing Calibration Verification (CCV). Calibration drift is measured during and at the end of the analytical sequence. The concentration of the CCV is calculated from the calibration curve and is compared to the true value. Run CCV's at a 10% frequency. Percent recovery must be 80-120%. If the CCV fails, re-analyze once. Failing to meet criteria again invalidates all samples in the sequence since the last acceptable CCV.

7. Continuing Calibration Blank (CCB). System contamination as well as calibration drift may affect the concentration value determined for the CCB. Run CCB's, immediately after the CCV's, at a 10% frequency. If the CCB fails, re-analyze once. If the CCB still fails to meet criteria, rerun all samples in the sequence since the last acceptable CCB.

   a. For AFCEE, the absolute value of the method blank may not exceed the RL.

   b. For SW-846 7000 series and Level III & IV, if the blank concentration is above the CRDL, the lowest concentration in the associated samples may not be less than 10x the blank concentration. If the lowest concentration is less than 10x the blank concentration or if the concentration of the blank is less than negative CRDL, re-analyze the samples

8. Matrix Spikes. Poor spike recovery may indicate a true matrix effect, poor sample homogeneity, inappropriate spike level or human error. If a true matrix effect is suspected, a post spike should be performed or if the native concentration is sufficiently high, a serial dilution should be performed.

   a. At least one MS must be processed per digestion batch or every 20 samples whichever is more frequent. The percent recovery limits are as follows:

      1) For AFCEE or Level III & IV, see project specific instructions.

      2) For SW-846 7000 series, 75-125%.

   b. At least one MSD must be processed per digestion batch or every 20 samples whichever is more frequent. Relative Percent Difference between MS and MSD must be <20%. The percent recovery limits are as follows:

      1) For AFCEE and Level III & IV, see project specific instructions.

      2) For SW-846 7000 series, 75-125%.

9. Laboratory Control Sample (LCS). One LCS is prepared for each digestion batch. Failure to meet acceptance criteria requires that all associated samples be redigested and reanalyzed. The percent recovery limits are as follows:

   a. For AFCEE and Level III & IV, see project specific instructions.

   b. For SW-846 7000 series, 80%-120%.

10. A Method Blank must be prepared for each digestion batch or every 20 samples whichever is more frequent. Failure to meet acceptance criteria requires that all associated samples be re-digested and re-analyzed.

    a. For AFCEE, no absolute value of the method blank may exceed the RL.

    b. For SW-846 7000 series and Level III & IV, if the blank concentration is above the CRDL, the lowest concentration in the associated samples may not be less than 10x the blank concentration. If the lowest concentration is less than 10x the blank concentration or if the concentration of the blank is less than negative CRDL, re-prep and re-analyze the samples.

11. A Serial Dilution tests for matrix interference. Perform a five-fold dilution on the selected sample. If the native concentration is at least 50 times the detection limit, the Relative Percent Difference between the native result and the calculated diluted result must be <10%.
12. A Post-digestion spike test for matrix interference. Recovery must be 85-115%.
    a. For AFCEE, perform a post-digestion spike only if serial dilution fails.
    b. For SW-846 7000 series and Level III & IV, a post-digestion spike is analyzed for each analytical batch.
13. Method of Standard Addition (MSA). If the pre-spike, post-digestion spike and serial dilution failed indicating a matrix effect, perform the analysis by MSA.

EQUIPMENT/APPARATUS

- Perkin Elmer AAnalyst 800 with an AS-800 autosampler.

REAGENTS

1. Concentrated Nitric acid.
2. Reagent water
3. Triton X – 100.
4. Matrix modifiers. Use 100ug Pd/ml-600ug $Mg(NO_3)_2$ from High Purity Standards. For Thallium analysis, dilute 1/10.
5. Standards. Each standard must have a unique ID, and all standard preparations must be documented in the standards logbook. All standard bottles must be labeled with its unique ID, name of the standard, concentration, date prepared, and expiration date. Unless otherwise specified, stock standards have expiration dates of 1 year after opening or date established by manufacturer. Standards are stored at room temperature on the bench or shelf.
    a. Working Standards.
        1) A stock solution at 1000 mg/L (ppm) is obtained from the manufacturer with the certificate of analysis from which the daily working standard is prepared.
        2) Working standard 1000 µg/L (ppb). Dilute 100µl of the stock solution to a final volume of 100 mL with a matrix of 2% HNO_3.
    b. Calibration Standards.
        1) All calibration standards associated with each analyte are specified under each element parameter page of the element file.
        2) Using the working standard stated above, prepare the calibration standards used by the instrument, daily.
    c. Initial calibration verification standard (ICV). ICV standards must be produced by a different supplier than the stock standard solution used for calibration standards.
        1) ICV stock standard solution at 25mg/L (ppm).
        2) ICV working standard, 50 µg/L (ppb). Dilute 0.2 mL of the standard to a final volume of 100 mL with a 2% HNO_3 matrix. Individual analyte ICV concentrations are prepared from the working standard at or near the mid-point of the calibration curve.

PROCEDURE

1. Warm up lamps for approximately 60 minutes. Each lamp has a recommended power setting according to the element.
2. Prepare daily standards for calibration.
3. Check the graphite tube to make sure it has not deteriorated. If the tube is changed, run condition tube program.

4. Clean the area where the graphite tube sits with Kimwipes™ and/or swabs. Make sure the optical windows are clean and free of dust.
5. Fill the rinse water container as needed. For every 500mLs of reagent water, add approximately 2-3mLs of a diluted Triton X solution.
6. Determine which samples are to be run and by what method.
7. See Table 1 for the analytical sequence.

CALCULATIONS

1. The following equations may be used to calculate the analytical results:

Equation 1. Calculation of sample concentration for aqueous samples.

$$\text{Sample concentration } (\mu g/L) = \frac{\text{Raw amount (from instrument, in } \mu g/L) \text{ x Digestate vol (L) x Dil. factor}}{\text{Sample amount (L)}}$$

In most cases, the Digestate volume and Sample amount are exactly the same, and thus cancel each other out.

In these situations, the equation reduces to :

Sample concentration ($\mu g/L$) = Raw amout (from instrument, in $\mu g/L$) x Dil. factor

Equation 1. Calculation of spike recovery.

$$\%R = \frac{\text{Conc. found in spike } (^{ug}/_{L}) - \text{Conc. found in native sample } (^{ug}/_{L})}{\text{Conc. spiked } (^{ug}/_{L})} \times 100$$

Where :

$$\text{Conc. spiked} = \frac{\text{Spiking standard concentration } (^{ug}/_{L}) \text{ x Volume spiked (mL)}}{\text{Amount of sample used for matrix spike (mL)}}$$

Equation 2. Calculation of relative percent difference between duplicates.

$$\%RPD = \frac{(\text{Raw amount found in the MS} - \text{Raw amount found in the MSD})}{(\text{Raw amount found in the MS} + \text{Raw amount found in the MSD})} \times 200$$

Equation 3. Calculation of postspike recovery.

$$\text{Postspike \% Recovery} = \frac{C_{POST}V_{POST} - C_{NAT}V_{NAT}}{C_{SPK}V_{SPK}} \times 100$$

Where :

C_{SPK} = Concentration of element present in the spike solution (ng/mL)

V_{SPK} = Volume of the spike solution added to the digestate (mL)

C_{POST} = Concentration of element determined from analysis after spiking (ng/mL)

V_{POST} = Volume of the postspike prepared for analysis (mL)

C_{NAT} = Concentration of element determined from analysis before spiking (ng/mL)

V_{NAT} = Volume of digestate to which spike was added (mL)

2. Method of Standard Addition (MSA). Samples may be calculated using the MSA technique as required. This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interference that causes a baseline shift. The method of standard additions should be used for analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

   a. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_X, are taken. To the first (labeled A) is added a known volume of V_S of a standard analyte solution of concentration C_S. To the second aliquot (labeled B) is added the same volume V_S of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_X is calculated:

$$C_X = \frac{S_B V_S C_S}{(S_A - S_B)V_X}$$

   Where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

   b. Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the

ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An Excel spreadsheet is available to calculate analytical results using the MSA technique.

c. For the results of this MSA technique to be valid, the following limitations must be taken into consideration:

1) The apparent concentration from the calibration curve must be linear over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve. If the slope is significantly different (greater than 20%), caution should be exercised.

2) The effect of the interference should not vary, as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

3) The determination must be free of spectral interference and corrected for nonspecific background interference.

REVIEW/VALIDATION

Analysts are to review and regress data daily. The supervisor or lead analyst performs final data review.

DOCUMENTATION

The analytical method and unique standard Ids must be documented in a logbook.

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

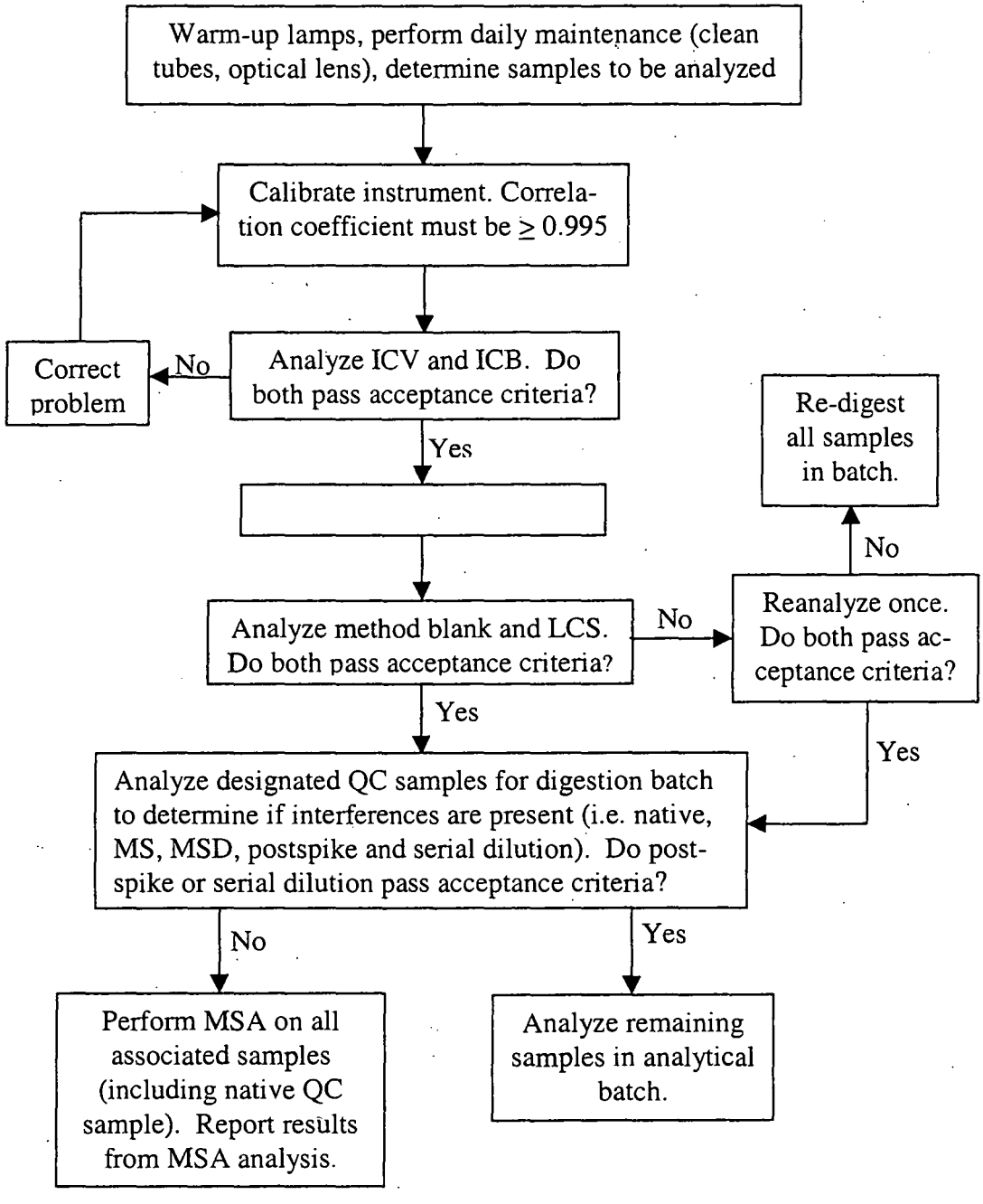
- Test Methods for Evaluating Solid Waste, Third Edition, SW-846, 7000-Series Methods.
- Air Force Center for Environmental Excellence (AFCEE) QAPP, version 3.0

Table 1. Analytical sequence for GFAA analysis.

Analysis	Description	Comments
BLANK	Calibration blank	Run blank first
STD1	Calibration standard	Run standards in ascending order
STD2	Calibration standard	
STD3	Calibration standard	
STD4	Calibration standard	
STD5	Calibration standard	
ICV	Initial Calibration Verification	• 90-110% • If the ICV fails, rerun once. If it still fails, recalibrate and re-analyze.
ICB	Initial calibration blank	Blank absolute value must be < RL.
PBW	Method blank	• For AFCEE, the absolute value of the blank must be < RL • For SW-846 7000 series and Level III & IV, if the blank concentration is above the CRDL, the lowest concentration in the associated samples may not be less than 10x the blank concentration. If the lowest concentration is less than 10x the blank concentration or if the concentration of the blank is less than negative CRDL, re-digest and re-analyze the samples.
LCS	Laboratory control sample	• For AFCEE and Level III & IV, see project instructions. • For SW-846 7000 series, 80-120%
S1	Sample 1	
S1pds	Sample 1 postspike	85-115%. For AFCEE, run if serial dilution fails.
S1ms	Sample 1 matrix spike	• For AFCEE and Level III & IV, see project instructions. • For SW-846 7000 series, 75-125%
S1msd	Sample 1 matrix spike duplicate	• For AFCEE and Level III & IV, see project instructions. • For SW-846 7000 series, 75-125% • Relative Percent Difference between MS and MSD, <20%
S1L	Sample 1 Serial Dilution	Diluted result must agree within ±10% of undiluted result if native result is >50 times the detection limit.
S2	Sample	
S3	Sample	
S4	Sample	
S5	Sample	
CCV	Continuing Calibration Verification	• 80-120% • If the CCV fails, rerun once. If it still fails, recalibrate and rerun all samples since the last valid CCV and CCB.
CCB	Continuing Calibration Blank	• For AFCEE, the absolute value of the blank must be < RL • For SW-846 7000 series and Level III & IV, if the blank concentration is above the CRDL, the lowest concentration in the associated samples may not be less than 10x the blank concentration. If the lowest concentration is less than 10x the blank concentration or if the concentration of the blank is less than negative CRDL, re-analyze the samples.
S6	Sample	
S7	Sample	
S8	Sample	
S9	Sample	
S10	Sample	
S11	Sample	
S12	Sample	

S13	Sample	
S14	Sample	
S15	Sample	
CCV	Continuing Calibration Verification	• 80-120% • If the CCV fails, rerun once. If it still fails, recalibrate and rerun all samples since the last valid CCV and CCB.
CCB	Continuing Calibration Blank	• For AFCEE, the absolute value of the blank must be < RL • For SW-846 7000 series and Level III & IV, if the blank concentration is above the CRDL, the lowest concentration in the associated samples may not be less than 10x the blank concentration. If the lowest concentration is less than 10x the blank concentration or if the concentration of the blank is less than negative CRDL, re-analyze the samples.

Figure 1. GFAA analysis scheme for all methods.



ARSENIC

1. **METHOD SW-846 7060A**
2. **INSTRUMENT** Perkin Elmer AAnalyst 800
3. **OPTIMUM CONCENTRATION RANGE:** 5-100 µg/L
4. **REPORTING LIMIT:** 1 µg/L
3. **SPIKING LEVELS**
   a. Matrix spike and Matrix spike dup: 50 µg/L
   B. Postspike: 50 µg/L
   C. **REAGENTS AND STANDARD SOLUTIONS**
   a. Calibration Standards: 5, 10, 25, 50, 100 µg/L
   b. Matrix Modifier: 1000ug Pd/ml-600ug $Mg(NO_3)_2$, HPS
   Amount added (by the instrument): 7.0 µL

6. **INSTRUMENT PARAMETERS (GENERAL):**

Furnace steps table.

Step #	Temp. (^{0}C)	Ramp Time	Hold Time	Internal Flow	Read Step
1	120	5	25	250	
2	140	3	30	250	
3	1300	5	30	250	
4	2100	0	5	0	X
5	2400	1	2	250	

a. Wavelength: 193.7nm
b. Slit: 0.70
C. Lamp Type: EDL

THALLIUM

2. **METHOD SW-846 7841A**
5. **INSTRUMENT** Perkin Elmer AAnalyst 800
6. **OPTIMUM CONCENTRATION RANGE:** 5-100 µg/L
7. **REPORTING LIMIT:** 1 µg/L
4. **SPIKING LEVELS**
   - d. Matrix spike and Matrix spike dup: 50 µg/L
   - E. Postspike: 50 µg/L
   - F. **REAGENTS AND STANDARD SOLUTIONS**
   - c. Calibration Standards: 5, 10, 25, 50, 100 µg/L
   - d. Matrix Modifier: 1000ug Pd/ml-600ug $Mg(NO_3)_2$, HPS. Dilute at a 1/10.

     Amount added (by the instrument): 5.0 µL

7. **INSTRUMENT PARAMETERS (GENERAL):**

Furnace steps table.

Step #	Temp. (^{0}C)	Ramp Time	Hold Time	Internal Flow	Read Step
1	120	5	20	250	
2	130	3	30	250	
3	900	5	40	250	
4	1600	0	5	0	X
5	2400	1	0	250	

- d. Wavelength: 276.8nm
- e. Slit: 0.70
- F. Lamp Type: EDL

PEL Laboratories, Inc. - Standard Operating Procedure

Sample Analysis: GC/MS Volatile Organics (SW-846 8260B/EPA 624)

APPROVED:

Volatiles Team Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. to determine the concentrations of selected volatile compounds in water, soil, and sediment samples by using purge-trap-desorb and gas chromatography/mass spectrometry (GC/MS) techniques per SW-846 method 8260B and EPA Method 624.

This SOP presupposes that the analyst has working knowledge and experience in the operation of purge-trap-desorb equipment, GC/MS equipment, and a GC/MS data system. Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Managers are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

The Reporting List may be found in Table 7. The compounds listed under the referenced method should be considered to be the standard reporting list for that method. Additional compounds may be added per client request. Reporting limits may be found in the Quality manual. These reporting limits will be proportionally higher for sample extracts and samples that require dilutions and soils with high moisture content when reported as dry weight. PEL does not analyze 2-Chloroethylvinyl ether (2-CEVE) as a standard compound; however, this compound may be added at the clients request. PEL runs the more stringent 8000 series method and the raw data/documentation will have the 8000 method listed, unless the client requests otherwise.

SUMMARY OF THE METHOD

Water samples are analyzed directly by bubbling Helium through a 5-mL or 25mL sample contained in a specially designed purging chamber at ambient temperature.

Soil and sediment samples are prepared and analyzed by one of two methods depending on the concentration of volatile components in the matrix. Low level solid samples are suspended in water and the suspension purged in a heated sparging chamber. High level solid samples are extracted with methanol, an aliquot of which is spiked into reagent water and purged at ambient temperature.

Purging efficiently transfers the volatile components in the different matrices from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column (analytical trap) where the volatiles are stripped from the purge gas. After purging is completed, the sorbent column is heated and back flushed with an inert gas directed into a gas chromatograph. The volatile components are thus transferred onto a chromatographic column which is temperature programmed to separate the compounds. As the compounds elute from the GC column, they pass through a heated transfer line into the mass spectrometer. The compounds are then ionized by electron impact, and the ion fragments are detected by an electron multiplier. The GC/MS data system then identifies the compounds by characteristic mass spectra and quantitates them via the internal standard method.

INTERFERENCES

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 analytical conditions by running laboratory reagent blanks. The use of non-Teflon plastic coating, non-Teflon thread sealants, or flow controllers with rubber components in the purging device should be avoided.

Samples can be contaminated by diffusion of volatile organics through the septum seal of VOA sample vials during shipment and storage. A trip blank prepared from organic-free water should be carried through sampling and analysis protocols to monitor contamination.

Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, the system is determined to be free of cross-contamination by checking subsequent sample analyses. If the target compound, which exceeded the calibration range, is detected in the subsequent analyses, all affected samples must be reanalyzed. The trap and other parts of the purging system are also subject to contamination. Frequent bake out and purging of the system may be required. The laboratory where analysis for volatile organics is conducted should be free of solvents, since they may be on the target analyte list.

QA/QC REQUIREMENTS

The holding time for the tests to which this SOP applies is 14 days for samples which have been shown to be acid-preserved to pH < 2, or 7 days if otherwise. If analyzing samples on the last day of holding time, the analyst should be aware that the sample should be analyzed within seven or fourteen 24-hour periods after sampling. Changes in time zones must be taken into account.

Samples must be prepared and analyzed as part of an analytical batch. An analytical batch is defined as a set of samples -- not to exceed 20 field samples -- of the same matrix that are prepared using the same techniques and reagents, are associated with a suite of QC samples, and are analyzed together in a continuous manner.

At times it may be necessary to break a batch. This implies that some of the samples in the batch are analyzed during a different or non-continuous time interval as the others, or on a different instrument. In these cases, the methanol extraction blank associated with that batch will be analyzed with the separated portions of the batch.

The following list describes QC parameters and requirements for this SOP:

1. The Qualitative and Quantitative sections of this SOP have additional requirements that must be observed.
2. Table 1 lists the characteristic ions for all target analytes, surrogates, and internal standards to which this SOP applies.
3. Instrument calibration
   a. Prior to initiating any data collection activities involving samples, blanks, or standards, it is necessary to establish that a given GC/MS system meets the instrument performance criteria. The purpose of this instrument performance check is to assure correct mass calibration, mass resolution, and mass transmission. This is accomplished through the analysis of 4-Bromofluorobenzene (BFB). The key ions produced during the analysis of BFB, and their respective ion abundance criteria are given in Table 2.
   b. An initial calibration curve consisting of a minimum of five-points will be analyzed to determine the linearity of response. Once the curve has been verified, analysis can proceed. A calibration standard from a source different to that used to obtain the initial calibration curve will be analyzed prior to the analysis of samples as an independent verification on the accuracy of the calibration standards. Acceptance criteria may be found in the **PROCEDURE** section of this SOP.
   c. A continuing calibration standard will be analyzed at the beginning of each 12-hour analytical sequence, prior to the acquisition of any samples.
   d. Initial and continuing calibration acceptance criteria may be found in the **PROCEDURE** section of this SOP.
4. Blanks
   a. System blanks are used to check the cleanliness of the analytical system (*i.e.,* GC/MS, purge-trap-desorb unit, etc.). A system blank will be analyzed after the continuing calibration standard, and prior to the analysis of any sample. The system blank consists of 5-mL or 25mL reagent water spiked with internal standards and surrogates.

b. Method blanks are used to verify the absence of contamination in the laboratory at the time during which samples were prepared or analyzed. For this SOP,
   i. The method blank for water analysis is the system blank described above analyzed at room temperature.
   ii. The method blank for low-level soil analysis is the system blank described above, with 5 grams of Ottawa sand added, and analyzed at 40°C.
   iii. The method blank for high-level soils consists of Ottawa sand extracted with methanol and treated thereafter as a regular sample. This blank is analyzed at room temperature. Each batch of samples prepared by methanol extraction should have an associated method blank.

c. Trip and field blanks are used to monitor contamination during sampling activities. These types of blanks are treated as a regular samples.

5. Laboratory Control Samples (LCS). These control samples are used to monitor analytical precision and accuracy, and are analyzed within the same batch as the Matrix Spike/Matrix Spike Duplicate (MS/MSD).
   a. The LCS for water analysis consists of 5-mL or 25mL reagent water spiked with internal standards, surrogates, and the target compounds.
   b. The LCS for solid samples consists of a 5-gram portion of Ottawa sand spiked with internal standards, surrogates, and the target compounds.
6. Matrix Spike/Matrix Spike Duplicate (MS/MSD).
   a. For every batch of samples of the same matrix, at least one sample must be spiked in duplicate. For 624, the frequency of spiking will be 10%.
   b. The spike level should be 20µg/Kg for soils, and 20 µg/L for water. *Special requirements may apply regarding spiking levels for samples used in support of compliance monitoring or samples that have high levels of target analytes.*
7. Surrogate spike.
   a. Each sample and QC sample analyzed will be spiked with surrogate compounds to monitor sample specific analytical performance.
   b. Surrogate recoveries must be within the range as stated for each method, or in the absence of specific limits, within ranges as determined by historical surrogate recovery data.
   c. If any sample exhibits surrogate recoveries outside these limits, the sample must be reanalyzed (and re-extracted if applicable). No specific acceptance criteria will be used for surrogate spikes to invalidate sample results because recovery of surrogates is frequently affected by matrix effects.
8. For Level I client work, citing a method, the method requirements have priority. However, when samples are analyzed under a project specific QAPP (i.e., AFCEE) the QA/QC criteria of that QAPP and the corrective actions listed have precedence for those select samples.

EQUIPMENT/APPARATUS

1. Sample Containers - 40 mL VOA vials with perforated screw cap. A Teflon-faced septum is placed inside the screw cap such that the Teflon-coated side comes into contact with the sample. The vials and septa are routinely purchased pre-cleaned (with certificate of analysis) from a commercial supplier and are not re-used.
2. Syringes - Hamilton gas tight syringes. Syringes used for standard solutions should be designated for such use and so marked (*i.e.,* color coding). Syringes used for samples may not be used for standards.
   a. Milliliter syringes – 5mL and 25mL.
   b. Microliter syringes - 10, 25, 50, 100, 250, 500, and 1,000 µL
3. Volumetric Flasks - assorted sizes, i.e.: 10, 25, 50, and 100 ml Class A.
4. Purge-trap-desorb system,
   a. Automated purge device for water sample analyses.
   b. Automated heated purge device for low-level soil/sediment sample analyses.
5. Gas Chromatograph (GC) - Analytical system suitable for temperature programming, the GC must be interfaced to a purge-trap system as described above, and have all required accessories for proper operation. Non-polytetrafluoroethylene (PTFE) thread sealants, or flow controllers with rubber components are not to be used.
6. Mass spectrometer (MS) - must be capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng of 4-Bromofluorobenzene is analyzed.

7. Data System - A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass, and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for non-target compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The software system must be capable of flagging all entries that have been manually edited by laboratory personnel.
8. Gas Chromatographic Columns. The laboratory may select their preferred columns based on known performance and previous experience.
9. Analytical trap - The trap should be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed with 1/3 each of Tenax, silica gel, and charcoal. (Alternate adsorbent traps may be used, depending on the volatility of the analytes of interest, and provided equivalent performance is demonstrated.)
10. Balance capable of measuring to 0.0001 g.

REAGENTS

1. Methanol - Purge and Trap grade, Burdick and Jackson or equivalent. Each separate lot of methanol (as designated by the vendor) must be demonstrated to be free of volatile target analyte contamination before use by analyzing 100-µL of methanol in 5-mL of reagent water. Reagent or organic-free water. Water in which an interferent is not observed at or above the reporting limits.
   a. Reagent water is obtained from a Milli-Q filtering system.
   b. When further cleanup of reagent water is required, the water is boiled for removal of common laboratory contaminants.
2. Ottawa sand
3. Standards. All volatile organic standards must be stored separately from other standards. Store Stock or working standards in Teflon-sealed screw-cap vials, or vials with stop-go caps, with minimal headspace at -10°C to -20°C.
   a. Stock Standard Solutions. Stock standard solutions are high concentration solutions used to prepare standards that will be used during the conduct of this SOP. Stock standard solutions have expiration dates of six months after opening, unless the expiration date is earlier than six months. All standards will be labeled with their unique ID, name of the standard, concentration, date prepared, and expiration date.
   b. The following is a list of all compounds/mixes used in the calibration curve, with the vendor name, product number, and concentration:
      Restek Internal standard mix-#56286- 25,000 ug/mL and #30074 – 2500 ug/mL
      Restek Surrogate standard mix- #30073-2500 ug/mL
      1. Restek trans-1,2-Dichloro-2-butene-#30274-2000 ug/mL
      2. Restek Carbon disulfide-#30258-2000 ug/mL
      3. Restek Ethyl methacrylate-#30289-2000 ug/mL
      4. Restek Custom Acrolein mix-#53472-2000 ug/mL
      5. Restek Acrylonitrile mix-#30246-2000 ug/mL
      6. Restek 502.2 Cal Mix #1-#30042-2000 ug/ml
      7. Restek 502.2 CAL 2000 Mega Mix-#30431-2000 ug/mL
      8. Restek Vinyl acetate-#30216-2000 ug/mL
      9. Restek Iodomethane-#30292-2000 ug/mL
      10. Restek Methyl-tert-butyl ether-#30402-2000µg/mL
      11. Restek 1-Chlorohexane-#57314-2000µg/mL
      12. Restek 1,1,2-Trichloro-1,2,2-Trifluoroethane-#30462-2000µg/mL
      13. Restek VOA Cal Mix#1-#30006-5000 ug/mL

      Secondary Source Standards *****
      14. AccuStandard 8260 Gas Mix M-#502B-10X/M601B-10X/M-502C-01-2000 ug/mL*****
      15. Accu Standard AppIX Volatiles Mix-#M8260- ADD-10X-2000 ug/mL
      16. AccuStandard 8260 Volatiles Mix-#M502A-R-10X-2000 ug/mL
      17. Accu Standard Acrolein -#APP-9-007-20X-2000µg/mL*****
      18. Accu Standard TCL Ketone Mix-#CLP-022K-10X-2000µg/mL*****

19. Accu Standard 1,1,2Trichloro-1,2,2-Trifluoroethane-#M-REF-14-10X-2000µg/mL*****
20. Accu Standard Methyl-tert-butyl ether-#S-078-10X-2000µg/mL*****
21. Accu Standard 1-Chlorohexane-#M-8010R-1-04-10X-2000µg/mL*****
22. Accu Standard Methyl Iodide-#APP-9-130-20X-2000µg/mL*****
23. Accu Standard Acrylonitrile-#APP-9-008-20X-2000µg/mL*****
24. Accu Standard Carbon disulfide-#APP-9-035-20X-2000µg/mL*****
25. Accu Standard Vinyl acetate-#APP-9-211-20X-2000µg/mL*****
26. Ultra Custom Standard-#CUS-2939-2000 ug/ml(Ethyl methacrylate and t-1,4-dc-2-b)*****
27. ***AccuStandardAppIX Volatiles Mix-#m8240C-R3-10X-varied concs.*****
28. ***AccuStandardChloroprene Mix-#APP-9-048-R1-10X-1000 ug/mL*****
29. ***Restek Benzyl chloride custom std.-#S5414-2000 ug/mL*****

***= Purchase in duplicate with different lot numbers.

c. Working Standard Solutions. Using the stock standard solutions, prepare the following working standard solutions by making appropriate dilutions in methanol. Working standard solutions have expiration dates of six months. All standards will be labeled with their unique ID, name of the standard, concentration, date prepared, and date of expiration.

i. Calibration Standards - Combine all target analytes (excluding surrogates and internal standards) in a methanol solution. The recommended concentration of the majority of target compounds is 50 µg/mL, while others may be at higher concentrations, usually due to differences in purging efficiencies.

The working standards for the calibration are prepared as follows:

Level	Conc (ppb)	Volume (mL)	Cal Mix/Gas Mix (µL)	AppIX Cal Mix (µL)	Acrolein Cal Mix (µL)	Ketone Cal Mix (µL)	Surr (µL)
1	2	100	4	4	10	10	0.5
2	5	100	10	10	20	20	1.0
3	10	100	20	20	50	50	2.0
4	20	50	20	20	30	30	4.0
5	50	25	25	25	20	20	10
6	60	10	12	12	30	30	12
7	80	10	16	16	40	40	16

For calibration through the water pathway of the Archon Autosampler levels 1 through 4 are prepared the same way. Levels 5 through 7 require the following preparation,

Level	Conc (ppb)	Volume (mL)	Cal Mix /Gas Mix(µL)	AppIX Cal Mix (µL)	Acrolein Cal Mix (µL)	Ketone Cal Mix (µL)	Surr (µL)
5	50	50	50	50	40	40	80
6	60	50	60	60	50	50	96
7	80	50	80	80	60	60	128

ii. Surrogate Spike - Combine all surrogate compounds in a methanol solution with a final concentration of 25 µg/mL. The recommended surrogate compounds are Toluene-d_8 , 4-Bromofluorobenzene, Dibromofluorobenzene and 1,2 Dichloroethane-d_4.

iii. Internal Standards - Combine all internal standards in a methanol solution with a final concentration of 25 µg/mL, and 250ug/mL. The recommended internal standards are Chlorobenzene-d_5, Fluorobenzene, and 1,4-Dichlorobenzene-d4. The higher concentration ISTD is used for auto addition by the Archon autosampler.

iv. Matrix Spike/Matrix Spike Duplicate– Solution containing all target compounds is prepared at a concentration of 10 ug/mL of Cal Mix and Appendix IX, and 25 ug/mL for Acrolein and Ketones. These solutions can also be used for the LCS.

v. Laboratory Control Sample - Prepare a spiking solution of the target compounds in a methanol solution at a concentration of 10 µg/mL of Cal Mix and Appendix IX, and 25 ug/mL for Acrolein and Ketones, respectively (Use the spiking solution).

PROCEDURE

1. Glassware and Equipment Cleaning
   a. The purging device should be rinsed daily by flushing methanol followed by water through the sample introduction inlet.
   b. Periodically, the autosampler may need to have either the soil or water sparge needle replaced.

2. Operating Conditions
   a. Gas Chromatograph - The instrumental operating conditions will be appropriate for the columns being used. The laboratory should maintain documentation regarding the columns and analysis conditions actually employed in that laboratory. The recommended operating conditions are listed in Table 4.
   b. Purge-Trap-Desorb - The flow rates for the purge-and-trap equipment and gas chromatograph are optimized for each system. However, recommended initial operating conditions are listed below and in Table 5.
      i. Purge flow: 35-40 mL/min. The purge flow should be verified when significant system changes are made.
      ii. Drypurge: 3 minutes, when the Vocarb 3000 trap is used, otherwise no dry purge
      iii. Purge time: 11 minutes
      iv. Desorb time: 2 minutes
      v. Desorb temperature: 250°C for the Vocarb 3000, 180 for the Tenax/silica gel trap.
      vi. Bake time: 8 minutes minimum
      vii. Bake temperature: 260°C for the Vocarb 3000 and 180 for the Tenax/silica gel trap.
      viii. Multi-port valve/transfer line temperatures: 150°C
   c. Mass Spectrometer - The required operating conditions are listed below and in Table 6.
      i. Electron Energy - 70 volts (nominal)
      ii. Mass Range - 35 - 300 amu
      iii. Scan time - to give at least 5 scans per peak, not to exceed 1 second per scan for capillary column.
      iv. Transfer Line Temperature - 200°C for Hewlett-Packard.
      v. Source Temperature - 130°C for Hewlett-Packard.

3. 4-Bromofluorobenzene (BFB) Calibration
   a. Requirements
      i. Prior to initiating any data collection activities involving samples, blanks, or standards, it is necessary to establish that a given GC/MS system meets the instrument performance criteria. The purpose of this instrument performance check is to assure correct mass calibration, mass resolution, and mass transmission. This is accomplished through the analysis of 4-Bromofluorobenzene (BFB). The key ions produced during the analysis of BFB, and their respective ion abundance criteria are given in Table 2.
      ii. The instrument must be calibrated using the same instrument conditions that are used to analyze the samples.
         1) Water and medium-to-high level soils must be quantified against calibrations performed by purging the calibration standards at ambient temperature.
         2) Low-level soils must be quantified against calibrations performed by purging the calibration standards at 40°C.
   b. Procedure
      i. Rinse a 5-mL gas-tight syringe with reagent water three times.
      ii. Fill the syringe with 5mL of reagent water.
      iii. When running in the soil pathway of the Archon autosampler, add 2 µL of the 25 µg/mL BFB solution directly into the open end of the syringe. Add the spiked water to a 40mL VOA vial nd cap tightly. When running through the water pathway, an entire 40 mL vial of water is used and 16 µL of the 25 ug/mL BFB solution is added.
      iv. Evaluate the BFB spectrum, determining if the ion abundances meet the criteria in Table 2. If the criteria are not met, further analysis is prohibited until corrective action has been taken and the problem resolved.

4. Initial Calibration

a. Requirements
   i. A calibration curve consisting of a minimum of five points will be analyzed to determine instrument sensitivity and the linearity of response. Once the curve has been verified, analysis can proceed. For Level I client work the low calibration standard is 2µg/L for soil pathway and 1µg/L for water pathway. When required, the lowest calibration point in the curve must be equal to or less than the reporting limit. In these cases, if the low-point is discarded from the calibration curve of any compound, the reporting limit for that compound must be increased to the appropriate level.
   ii. Calculating the relative response factor of the Xylenes requires special attention. On capillary columns, the m- and p-Xylene isomers coelute. Therefore, when calculating the relative response factor, remember this peak represents twice the concentration of the o-Xylene peak. The instrument must be calibrated using the same instrument conditions that are used to analyze the samples.

b. Procedure (Soil Pathway)
   i. Rinse a 5 mL gas-tight syringe with reagent water three times.
   ii. Fill the syringe with 5mL of a standard prepared as directed in Reagent Section (3.c.i).
   iii. Add the 5 mL of prepared standard to a 40 mL vial being sure to replace cap tightly.
   iv. Label the vial with the standard concentration.
   v. Repeat steps for each standard.

c. Procedure (Water Pathway)
   i. Completely fill a 40 mL vial with a standard prepared as directed in Reagent Section (3.c.i).
   ii. Cap vial tightly ensuring that no headspace is present.
   iii. Label the vial with the standard concentration.
   iv. Repeat steps for each standard.

d. Evaluation of the curve.
   i. Calculate the relative response factor (RRF) for each target compound using Equation 2.
   ii. Calculate the average relative response factor for each compound.
   iii. Calculate the percent relative standard deviation (%RSD) using Equation 3.
   iv. Compare the %RSD value to the %RSD requirements of sections 6 and 7 below. The calculated %RSD must not exceed the maximum value for the target compounds. If this criterion is not met, the calibration curve is invalid and must be regenerated with new calibration points or analytical standards.
   v. Some compounds have minimum average RRF requirements that must also be met. Refer to Table 3.
   vi. Linearity - If the %RSD of any compound is 15% 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.
   vii. If the %RSD of any compound is greater than 15%, the analyst may review the results for these analytes to ascertain if the problem is associated with one of the calibration standards. Alternatively, the averaging method can be used as cited in Update 3 of SW-846 Method 8260. No analytes can have an RSD greater than 40%, and no more than 5% of the compounds can have an RSD of greater than 30%.

5. Continuing Calibration
   a. Requirements
      i. A continuing calibration standard selected from the middle of the initial calibration range, or as specified by the method, will be analyzed at the beginning of each 12-hour analytical sequence and prior to the analysis of any samples. The instrument must be calibrated using the same instrument conditions that are used to analyze the samples.
      ii. For each analyte, calculate the %Difference between the RRF of the continuing calibration standard, and the average RRF from the initial calibration curve using Equation 4.
         1) The %Difference must be less than 20%. Alternatively, the averaging method can be used as cited in Update 3 of SW-846 Method 8260. The average must be less than 15%, no analytes can have an RSD greater than 40%, and no more than 5% of the compounds can have an RSD of greater than 30%.
         2) Some compounds have minimum average RRF requirements that must also be met. Refer to Table 3.
         3) If the criteria are not met, further analysis is prohibited until corrective action has been taken and the problem resolved.

b. Procedure (Soil and Water Pathways)
   i. The required additions of surrogate and standard solutions for each matrix pathway are located in the front each instrument book under "8260 50CC Standard Preparation".
   ii. Calculate the RRF for each of the target compounds found using Equation 2.

6. System Blanks
   a. Requirements
      i. A system blank will be analyzed at the beginning of each 12-hour analytical sequence and prior to the analysis of any samples. It must be analyzed after the calibration standard to ensure that there is no carryover of material from the standards into samples.
      ii. The system blank may not contain any target analyte at a concentration above the reporting limit. If the system blank exceeds these criteria, corrective action must be taken and documented.
      iii. The system blank must be analyzed using the same instrument conditions that are used to analyze the samples.
      iv. Review the requirements in Sections 10 and 11, "Qualitative Analysis" and "Quantitative Analysis" before proceeding.
   b. Procedure (Soil Pathway)
      i. Rinse a 5-mL gas-tight syringe with reagent water three times.
      ii. Fill the syringe with 5mL of reagent water.
      iii. Add 10 µL of the surrogate solution to the open end of the syringe.
      iv. Add this solution to a 40 mL vial and cap the vial tightly.
   c. Procedure (Water Pathway)
      i. Fill a 40 mL vial with reagent grade water. Cap vial tightly making sure that no headspace is present within the vial.
      ii. Inject 80 µL of surrogate solution into vial through the septa and invert vial 3 times.

7. Water Samples
   a. Requirements
      i. All samples, standards, and QC check samples must be analyzed at room temperature.
      ii. A continuing calibration standard must be analyzed and pass criteria before sample analysis can proceed.
      iii. A system/method blank must be analyzed and pass criteria before sample analysis can proceed.
      iv. A matrix spike/matrix spike duplicate must be analyzed for every batch of up to 20 samples. The sample selected for spiking should have been analyzed in the batch.
      v. A Laboratory Control Sample should be analyzed with the same 12-hours the matrix spike/matrix spike duplicate.
      vi. Review the requirements in Sections 10 and 11, "Qualitative Analysis" and "Quantitative Analysis" before proceeding.
   b. Procedure
      i. Check vial for any headspace. If headspace is present, note on queue sheet and notify supervisor.
      ii. Inject 80 µL of surrogate solution into the vial through the septa and invert 3 times.
      iii. Allow all samples to come to ambient temperature before analysis.
      iv. Calculate sample concentrations of the target analytes using Equation 7.
         1) Sample concentrations are calculated against a calibration curve analyzed at ambient temperature.
         2) All target analytes detected must be no greater than 10% above the linear calibration range established for the instrument. If a target analyte exceeds this limit, the sample must be diluted.
         3) For SW-846 8260, when linearity exists, calculations are performed using the average relative response factor from the initial calibration curve. Alternatively, the regression line fitted to the initial calibration may be used for determination of analyte concentration.
      v. Calculate surrogate recoveries using Equation 7.
      vi. Matrix spikes - One sample in the batch is selected for matrix spiking. The sample is analyzed as indicated above, followed by two aliquots of the same sample, which are spiked with secondary source standards as indicated on the front of each instrument book under "8260 LCS/MS/MSD Preparation"
         1) Calculate the recovery (%R) for each target analyte of each matrix-spiked sample as compared to the unspiked sample using Equation 8.

2) Calculate the relative percent difference (RPD) for each target analyte between the two spiked samples using Equation 9.

vii. Laboratory Control Sample - An aliquot of blank reagent water is spiked with secondary source standards as indicated on the front of each instrument book under "8260 LCS/MS/MSD Preparation".

1) Calculate the recovery (%R) for each target analyte of each matrix spiked sample as compared to the unspiked sample using Equation 8.

8. Low-Level Sediment/Soil Samples by Heated Purge-Trap-Desorb

a. Requirements

i. All samples, standards, blanks, and QC check samples must be analyzed at 40°C.

ii. A continuing calibration standard must be analyzed and pass criteria before sample analysis can proceed.

iii. A system/method blank must be analyzed and pass criteria before sample analysis can proceed.

iv. Matrix spikes must be analyzed for every batch of up to 20 samples.

v. A Laboratory Control Sample should be analyzed immediately after the MS/MSD.

vi. When required, the % Moisture of all soil samples is to be determined (SOP00035-WC, Determination of Percent Moisture).

vii. All balances used during the analysis of samples must be calibrated according to SOP00008-QA, Analytical Balance Operation.

viii. Review the requirements in Sections 11 and 12, "Qualitative Analysis" and "Quantitative Analysis" before proceeding.

b. Procedure

i. Tare a 40 mL vial (including cap) with 5 ml of water in it plus a stir bar.

ii. Homogenize the sample using a wooden disposable spatula and transfer 0.5 to 5 grams of the sample to the tared 40 mL vial; if the sample was collected in an EnCore sampler, transfer the aliquot with the EnCore tool to the vial. The smallest sample size permitted for this method is 0.5 gram. Cap vial and weigh.

iii. Enter all pertinent data into the Soil Sample Prep Log, immediately, recording the weight of the vial to an accuracy of 0.0001. Label the vial with sample number and weight of the sample.

iv. If the sample is to be analyzed immediately proceed the following steps. If the sample is to be set aside for analysis at a later date place the vial along with any other associated samples in a labeled box within Refrigerator C of the Volatiles Laboratory. Frozen vials must be thawed prior to analysis.

v. Add 10 µL of the surrogate solution through the septa of the vial.

vi. Calculate sample concentrations of the target analytes using Equation 10.

1) Sample concentrations are calculated against a calibration curve analyzed at 40°C.

2) All target analytes detected must be no greater than 10% above the linear calibration range established for the instrument. If a target analyte exceeds this limit, the sample must be diluted.

3) For SW-846 8260, when linearity exists, calculations are performed using the average relative response factor from the initial calibration curve. Alternatively, the regression line fitted to the initial calibration may be used for determination of analyte concentration.

vii. Calculate surrogate recoveries using Equation 7.

viii. Matrix spikes – If the client has designated a sample to be used as a matrix spike it is analyzed as indicated above, followed by two aliquots of the same sample, which are spiked using the seconddard standard mix. This is done by spiking the water that is mixed with the sample with the secondary source solution, as well as surrogate solution. If no sample is available for matrix spike, MS/MSD is prepared using reagent grade water and 5 grams of Ottawa sand.

1) Calculate the recovery for each target analyte of each matrix spiked sample as compared to the unspiked sample using Equation 8.

2) Calculate the relative percent difference for each target analyte between the two spiked samples using Equation 9.

ix. Laboratory Control Sample - An aliquot of blank reagent water is spiked with the secondary source solution and surrogate.

1) Calculate the recovery for each target analyte of each matrix spiked sample as compared to the unspiked sample using Equation 8.

9. High Level (>1,000 µg/Kg) Sediment/Soil Samples by Methanol Extraction
   a. Requirements
      i. All samples, standards, blanks, and QC check samples must be analyzed at ambient temperature.
      ii. A total of 100 µL of methanol must be added to all samples. The total volume of methanol added does not include any spikes contained in methanol added to the water, such as standards and samples. If 100 µL of a sample is analyzed, no make up methanol need be added. But if 70 µL of a sample is analyzed, a makeup volume of 30 µL of methanol must be added.
      iii. For each batch of samples extracted by this method, a portion of the methanol used must be transferred to a vial and treated thereafter as a sample. This is the method blank.
      iv. A continuing calibration standard must be analyzed and pass criteria before sample analysis can proceed.
      v. A system blank must be analyzed and pass criteria before sample analysis can proceed.
      vi. Matrix spikes must be analyzed for every batch of up to 20 samples.
      vii. A Laboratory Control Sample (LCS) must be analyzed within the same 12-hours as the MS/MSD.
      viii. All operations with the sample should be expedited to minimize loss of target analytes. It is recommended that cold samples be used.
      ix. When required, the % Moisture of all soil samples must be determined.
      x. Review the requirements in Sections 11 and 12, "Qualitative Analysis" and "Quantitative Analysis" before proceeding.
   b. Procedure
      i. Tare a 40 mL vial with 9 mL of methanol.
      ii. Homogenize the sample using a disposable wooden spatula and transfer 0.5 to 5 grams of the sample to the tared 40 mL vial; if the sample was collected in an EnCore sampler, transfer the aliquot with the EnCore tool to the vial. Enter all pertinent data into the Soil Sample Prep Log, immediately, recording the weight of the vial to an accuracy of 0.0001. Label the vial with sample number and weight of the sample.
      iii. Add 1.0 mL of the 25 µg/mL surrogate standards solution to the sample. Cap the vial and sonicate for 15 minutes. Record the surrogate solution VOS# in the comments section of the Soil Sample Prep Log. Transfer 2-mL of the extract to an amber GC vials and label amber vial with the sample number. If the sample is not going to be analyzed immediately, store at 4°C.
      iv. Soil Pathway
         1) Rinse a 5-mL gas tight syringe with reagent water three times.
         2) Fill the syringe with 5mL of reagent water.
         3) Add 100 µL of the sample extract (or other volume as determined by the sample screening process) to the open end of the sample-filled syringe. Add the makeup volume of methanol (enough to complete 100 µL of methanol added to water).
         4) Add this to a 40 mL vial and cap tightly.
      v. Water Pathway
         1) Fill a 40 mL vial with reagent grade water leaving 1 to 2 mL of headspace.
         2) Inject 800 µL of extract into vial
         3) Fill remaining space in vial with reagent grade water being careful not to overfill the vial.
         4) Cap tightly and invert 3 times.
      vi. Calculate sample concentrations of the target analytes using Equation 11.
         1) If any volume less than 100 µL of the sample extract is analyzed, the ratio between 100 µL and the actual volume used is the dilution factor.
         2) Any additional dilution must be multiplied by the dilution factor.
         3) Sample concentrations are calculated against a calibration curve analyzed at ambient temperature.
         4) All target analytes detected must be within the linear calibration range established for the instrument.
         5) If a target analyte exceeds the calibration range, the volume of sample extract analyzed must be adjusted in such a manner that response of the constituents found are within the calibration range.

6) For SW-846 8260, when linearity exists, calculations are performed using the average relative response factor from the initial calibration curve. Alternatively, the regression line fitted to the initial calibration may be used for determination of analyte concentration.

vii. Calculate surrogate recoveries using Equation 7.

viii. Matrix spikes - If the client has designated a sample to be used as a matrix spike it is analyzed as indicated above, followed by two aliquots of the same sample. The two additional aliquots of the same sample are also spiked with secondary source solution, added to the sample immediately after adding the surrogate standards spiking solution. Add 8.0 mL of methanol to the vial containing the matrix spiked samples. Cap the vials and sonicate for 15 minutes. Transfer 2-mL of the extract to an amber GC vials and store or analyze. If no MS/MSD has been designated by the client, blank spikes are prepared at the bench as indicated on the front of each instrument book under "8260 LCS/MS/MSD Preparation" and then analyzed.

1) Calculate the recovery (%R) for each target analyte of each matrix spiked sample as compared to the unspiked sample using Equation 8.

2) Calculate the relative percent difference (RPD) for each target analyte between the two spiked samples using Equation 9.

ix. Laboratory Control Sample – Prepared at the bench as indicated on the front of each instrument book under "8260 LCS/MS/MSD Preparation"

1) Calculate the recovery (%R) for each target analyte of each matrix spiked sample as compared to the unspiked sample using Equation 8.

10. Reanalysis of Samples

a. In analytical chemistry, reanalysis of samples is often the rule rather than the exception. When requested by the client, sample results which are generated from a reanalysis will be identified as such by using suffixes.

b. The original analysis of any sample, or the most concentrated of two dilutions, will not have a suffix.

c. All subsequent reanalysis of any given sample will be given a suffix, which is added to the end of the Lab Sample ID number. The suffixes are as follows:

i. DL is used for samples that are reanalyzed at a higher dilution than the original. Thus, if sample M1234001 is analyzed at a dilution of 1:10, the Lab Sample ID for the reanalysis is M1234001DL1.

ii. RE is used for samples that are reanalyzed at the same dilution as the original analysis. Reasons for this may include poor surrogate recovery during the first analysis, questionable carryover from a previous sample, etc. The first analysis of sample M1234001 uses the sample number as the Lab Sample ID. If the analysis of M1234001 had poor surrogate recoveries and must be reanalyzed, the Lab Sample ID of the reanalysis is M1234001RE1.

d. Reasons for reanalysis (with or without dilution):

i. A sample will be reanalyzed when the percent recovery a surrogate is outside criteria.

ii. A sample will be reanalyzed when the area of any internal standard is outside criteria.

iii. A sample will be diluted and reanalyzed when a requested target compound exceeds calibration range.

iv. A sample will be reanalyzed, more concentrated, when a requested target compound, for which the sample was originally diluted, is significantly below the mid-point of the calibration curve.

11. Qualitative Analysis

a. The Target compounds listed in Table 1, shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

i. For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the same component in the most recent continuing calibration standard. For reference, the standard must be run in the same 12-hour time period as the sample. If samples are analyzed during the same 12-hour time period as the initial calibration standards, use the RRT values from the calibration point with the concentration equal to the daily or continuing standard. The RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest as given in Table 1.

ii. For comparison of standard and sample component mass spectra, the mass spectra of each should be obtained on the same GC/MS. Once obtained, these standard spectra may be used for identification purposes, only if the GC/MS meets the daily instrument performance requirements for BFB. These standard spectra may be obtained from the run used to obtain reference RRTs.

iii. The requirements for qualitative verification by comparison of mass spectra are as follows:
   1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.
   2) The relative intensities of ions specified in the preceding paragraph must agree within ± 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent).
   3) Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra.

iv. If a compound cannot be verified by all of the above criteria, but in the technical judgment of the analyst and reviewer, the identification is correct, then the analyst shall report that identification and proceed with quantification.

b. A library search may be executed for non-target sample components for the purpose of tentative identification. For this purpose, the most recent available release of the NIST/EPA/MSDC mass spectral library, shall be used. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

i. Up to 10 organic compounds of greatest apparent concentration not listed in the client specific compound list, excluding the system monitoring compounds, shall be tentatively identified via a forward search of the NIST/EPA/MSDC Library (substances with responses less than 10% of the nearest internal standard are not required to be searched in this fashion). Only after visual comparison of sample spectra with the nearest library searches will the mass spectral analyst assign a tentative identification. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

ii. Guidelines for making tentative identification:
   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.
   2) The relative intensities of the major ions should agree within ± 20% (Example: For an ion with an abundance of 50 percent of the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)
   3) Molecular ions present in reference spectrum should be present in sample spectrum.
   4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.
   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 co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

iii. If, in the technical judgment of the mass spectral analyst, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral analyst should give additional classifications of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

12. Quantitative Analysis

a. Target components identified shall be quantified by the internal standard method. The internal standard used shall be that which is assigned in Table 7. The EICP area of the characteristic ions of analytes listed in Table 1, are used.

b. Internal standard responses and retention times in all standards, blanks, samples, and QC samples, must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (or 12-hour) calibration standard, the chromatographic system must be inspected for malfunctions, corrections made as required, and for samples analyzed during the same time period as the initial calibration standards, compare the internal

standard responses and retention times against the mid-point calibration standard or average RRF, depending on the analytical method. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

i. If after reanalysis, the EICP areas for internal standards are inside the acceptance limits (-50% to +100%), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, submit only data from the analysis with EICPs within the acceptance limits. This is considered the initial analysis and must be reported as such on all data deliverables.

ii. If the reanalysis of the sample does not solve the problem, i.e., the EICP areas are outside the limits for both analyses, then submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables.

c. The concentration of the target compound is calculated following the equations in the next section. When linearity exists, calculations are performed using the average relative response factor from the initial calibration curve. Alternatively, the regression line fitted to the initial calibration may be used for determination of analyte concentration.

d. When target compounds are below the reporting limit, but are above the MDL and the spectra meet the identification criteria , report the concentration with a "J" qualifier. For example, if the reporting limit is 10 µg/L and a concentration of 3 µg/L is calculated, report as "3J."

e. Xylenes (o-, m-, and p- isomers) are to be combined and reported as Xylenes (total). Because the m- and p-Xylene isomers coelute on capillary columns, special attention must be given to the quantitation of the Xylenes. The areas of the two peaks may be summed, and the concentration determined, or the concentration represented by each of the two peaks may be determined separately, and then summed. In quantitating sample concentrations, depending on the method, use the RRF from the o-Xylene isomer only or from a RRF determined by summing both Xylene peak areas. It is required that all three Xylene isomers be present in the initial and continuing calibration standards.

f. The cis and trans stereoisomers of 1,2-Dichloroethene are to be combined and reported as 1,2-Dichloroethene (total). Use the single RRF value to determine the concentration. The areas of the two peaks may be summed and the concentration determined, or the concentration represented by each of the two peaks may be determined separately, and then summed. It is required that both the cis and trans isomers of the 1,2-Dichloroethene be present in the initial and continuing calibration standards.

g. If the on-column concentration of any compound in any sample exceeds the initial calibration range by more than 10%, a new aliquot of that sample must be diluted and purged. Guidance in performing dilutions, and exceptions to this requirement are given below.

i. Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

ii. The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

iii. For total Xylenes, where three isomers are quantified as two peaks, the calibration of each peak, should be considered separately, i.e., a diluted analysis is not required for total Xylenes unless the concentration of the peak representing the single isomer exceeds 88 µg/L, or the peak representing the two coeluting isomers on the GC column exceeds 176 µg/L. For the cis and trans isomers of 1,2-Dichloroethene, a diluted analysis is not required unless the concentration of either peak exceeds 88 µg/L.

h. Calculate the recovery of each system monitoring compound in all samples, blanks, matrix spikes, and matrix spike duplicates. Determine if the recovery is within limits (Table 3), and report on the appropriate form.

i. Calculate the concentrations of the system monitoring compounds using Equation 7.

ii. If the recovery of any one system monitoring compound is not within the stated limits (Table 3), the following are required:

- Check to be sure that there are no errors in calculations, formulation of the system monitoring compound spiking solutions, and internal standards. Also check instrument performance. Additionally, verify proper software algorithms and proper integration of peak area.
- Reanalyze the sample if none of the above steps reveal a problem.
- If an undiluted analysis with acceptable monitoring compound recoveries is being submitted, do not reanalyze diluted samples if the system monitoring compound recoveries are outside the limits.
- Never reanalyze the matrix spike or matrix spike duplicate (MS/MSD), even if the system monitoring compound recoveries are outside the limits. *Note:* This does not apply if there is an obvious error in adding the proper amount of spiking solution, or if there is a bad purge.
- If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications, it should be reanalyzed only if the MS/MSD system monitoring compound recoveries are within the limits. If the sample and associated MS/MSD show the same pattern (i.e., outside the limits), then the sample does not require reanalysis and a reanalysis does not need to be submitted.

iii. If the reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, submit only data from the analysis with system monitoring compound recoveries within the limits. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

iv. If the reanalysis of the sample does not solve the problem (i.e., the system monitoring compound recoveries are outside the limits for both analyses), then submit the data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables. Refer to the **PROCEDURE** section where the reanalysis of samples is discussed.

v. If the recovery of any one system monitoring compound in a method blank is outside the limits, then the method blank and all associated samples must be reanalyzed.

i. Calculate spike recoveries in the LCS, MS and MSD

i. Calculate the concentrations of the matrix spike compounds using Equation 8.

ii. Calculate the relative percent difference (RPD) of the recovery for each compound in the matrix spike and matrix spike duplicate using Equation 9.

iii. The limits for matrix spike compound recovery and RPD are given in Table 4.

CALCULATIONS

$$\text{Calibration spike volume } (\mu L) = \frac{\text{Target mass on-column } (ng)}{\text{Concentration of standard solution } (\mu g / mL)} \times \frac{1000\ \mu L / mL}{1000\ ng / \mu g}$$

Equation 1. Calculation of calibration standard spike volume for GC/MS VOA calibration.

$$RRF = \frac{\text{Area of target analyte}}{\text{Area of internal standard}} \times \frac{\text{Mass on-column of internal standard}}{\text{Mass on-column of target analyte}}$$

Equation 2. Calculation of relative response factors (RRF).

$$\%RSD = \frac{\text{Standard deviation from RRF distribution}}{\overline{RRF}} \times 100$$

Equation 3. Calculation of %RSD.

$$\%Diff = \frac{RRF - \overline{RRF}}{\overline{RRF}} \times 100$$

Equation 4. Calculation of %Difference for continuing calibration standards.

$$\text{Raw amount (ng on - column)} = \frac{\text{Response - Intercept}}{\text{Slope}} = \left(\frac{\text{Area of target compound}}{\text{Area of internal standard}}\right) x \left(\frac{\text{Mass of internal standard (ng)}}{\overline{RRF} \text{ or } RRF_{\text{Daily standard}}}\right)$$

Equation 5. Calculation of raw amount.

$$\text{Sample concentration } (\mu g / L) = \frac{\text{Raw amount (ng) x Dil. factor}}{\text{Volume purged (mL)}} x \left(\frac{0.001 \mu g / ng}{0.001 L / mL}\right)$$

Equation 6. Calculation of concentration in water samples.

$$\text{Surrogate recovery (\%)} = \frac{\text{Raw amount found (ng)}}{\text{Amount spiked (ng)}} \times 100$$

Equation 7. Calculation of surrogate recovery.

$$\%R = \frac{\text{Raw amount found in matrix spike (ng) - Raw amount found in native sample (ng)}}{\text{Amount spiked (ng)}} \times 100$$

Equation 8. Calculation of matrix spike and LCS recovery.

$$\%RPD = \frac{(\text{Raw amount found in the MS - Raw amount found in the MSD})}{(\text{Raw amount found in the MS + Raw amount found in the MSD})} \times 200$$

Equation 9. Calculation of relative percent difference between duplicate matrix spikes.

$$\text{Sample concentration } (\mu g/Kg) = \frac{\text{Raw amount (ng) x Dil factor}}{\text{Weight of sample analyzed (g) x } \%Solids/100} x \left(\frac{0.001 \ \mu g/ng}{0.001 \ Kg/g}\right)$$

Equation 10. Calculation of target analyte concentration in low level soil samples.

$$\text{Sample concentration } (\mu g/Kg) = \left(\frac{\text{Raw amount (ng) x Dil. factor}}{\text{Weight of sample analyzed (g) x } \%Solids/100}\right) x \left(\frac{\text{Total extract volume (mL)}}{\text{Volume of extract analyzed (mL)}}\right) x \left(\frac{0.001 \ \mu g/ng}{0.001 \ Kg/g}\right)$$

Equation 11. Calculation of target analyte concentration in high level soils.

REVIEW/VALIDATION

Data review and validation must be reviewed by the section supervisor according to PEL Laboratories, Inc.'s Quality Manual. Refer to the Data Review and Validation SOP for detailed instructions, SOP00085-QA.

DOCUMENTATION

Refer to SOP00040-QA for general laboratory rules for documentation.

All analyses will be documented in a logbook. Each logbook will be uniquely identified, and each page within each logbook will have a unique page number. Refer to SOP00077-V for detailed instructions.

All standards preparation must be documented in a standards logbook. Please follow the guidelines given in the logbook. All standards and reagents must be labeled with the date of preparation, preparer's initials, PEL unique ID, concentration of solution and expiration date.

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves, oven mitts, and lab coats are a minimum requirement. Other measures to be considered are that standards must be prepared under the charcoal filter hood, no open flames, gas cylinders must be chained securely, glassware must be handled carefully, and no food or open drink containers should be in the working laboratory.

Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

POLLUTION AND PREVENTION

Pollution and Prevention encompasses any technique that reduces or eliminates the quantity and/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

For more information about pollution prevention consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477

WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable Federal, state, and local rules and regulations. 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 sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult The Waste Management Manual for Laboratory Personnel available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477

REFERENCES

- *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods* SW-846 (3rd Edition) Method 8260
- *EPA method 624,* 40 CFR, part 136, 7-1-94 edition
- PEL Laboratories, Inc. Quality Manual

Table 1. Characteristic Ions For Volatile Target Compounds, Surrogate Compounds and Internal Standards.

Volatile Compounds	Primary Ion	Secondary Ion(s)

Volatile Compounds	Primary Ion	Secondary Ion(s)
Acetone	43	58
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Benzene	78	52, 71
Benzyl chloride	91	126, 65,128
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 129
Bromoform	173	171, 175, 252
Bromomethane	94	96, 79
2-Butanone[b]	43	57, 72
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-butylbenzene	119	91, 134
Carbon Disulfide	76	78, 44
Carbon tetrachloride	117	119, 121
Chlorobenzene	112	114, 77
Chloroethane	64	66, 49
Chloroform	83	85, 47
Chloromethane	50	52, 49
Chloroprene	88	53, 90, 51
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
Dibromochloromethane	129	127,208, 206
1,2-Dibromo-3-chloropropane	157	75, 155, 77
1,2-Dibromoethane	107	109, 93, 188
Dibromomethane	93	174, 95
trans-1,4-Dichloro-2-butene	75	53, 89
1,2-Dichlorobenzene	146	148, 111, 113
1,3-Dichlorobenzene	146	148, 111, 113
1,4-Dichlorobenzene	146	148, 111, 113
Dichlorodifluoromethane	85	87, 101
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	64, 98
1,1-Dichloroethene	96	61, 98
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	62, 41
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,4-Dioxane	88	58, 43, 57
Ethylbenzene	106	91
Ethyl methacrylate	69	41, 39, 99
2-Hexanone	43	58, 57, 100
Hexachlorobutadiene	225	223, 227
Iodomethane	142	127, 141
Isobutyl Alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Methacrylonitrile	41	67, 39, 52

Volatile Compounds	Primary Ion	Secondary Ion(s)
Methylene Chloride	84	49, 51, 86
Methyl Methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	43	58, 100
Naphthalene	128	127,129
Propionitrile	54	49, 89, 91
n-Propylbenzene	91	120
Styrene	104	78, 103
1,1,1,2-Tetrachloroethane	131	133, 117, 119
1,1,2,2-Tetrachloroethane	83	85, 131, 133
Tetrachloroethene	164	129, 131, 166
Toluene	91	92, 65
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1-Trichloroethane	97	99, 117
1,1,2-Trichloroethane	97	83, 85, 99
Trichloroethene	130	95, 97, 132
Trichlorofluoromethane	101	103, 66
1,2,3-Trichloropropane	75	110, 77, 61
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl Acetate	43	86
Vinyl Chloride	62	64, 61
m-,p-Xylene	106	91
o-Xylene	106	91
Methyl-tert-butyl ether	73	57
1,1,2-Trichloro-1,2,2-trifluoeoethane	101	151, 103
1-Chlorohexane	91	55, 56
Internal Standards	**Primary Ion**	**Secondary Ion(s)**
Bromofluorobenzene	95	174, 176
Dibromofluoromethane	113	111,192
Toluene-d_8	98	70, 109
1,2 Dichloroethane-d_4	102	65,67
Internal Standards	**Primary Ion**	**Secondary Ion(s)**
Fluorobenzene	96	70,50
Chlorobenzene-d_5	117	82,119
1,4-Dichlorobenzene-d_4	152	150,115

Table 2. BFB ion abundance criteria for 8260

Mass	Ion Abundance Criteria
50	15.0 to 40.0 percent of mass 95
75	30.0 to 60.0 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5.0 to 9.0 percent of mass 95

173	Less than 2.0 percent of mass 174
174	Greater than 50.0 percent of mass 95
175	5.0 to 9.0 percent of mass 174
176	Greater than 95.0 percent but less than 101 percent of mass 174
177	5.0 to 9.0 percent of mass 176

Table 3. SW-846 8260 Relative Response Factor Criteria For Initial and Continuing Calibration of Volatile Organic Compounds.

Calibration Check Compounds (CCC)

Volatile Compounds	Minimum RRF	Maximum % RSD	Maximum % Difference
Chloroform	----	30	20
1,1-Dichloroethene	----	30	20
1,2-Dichloropropane	----	30	20
Ethylbenzene	----	30	20
Toluene	----	30	20
Vinyl Chloride	----	30	20

System Performance Check Compounds (SPCC)[a]

Volatile Compounds	Minimum RRF for 8260	No Maximum % RSD or %D
Bromoform	0.100	----
Chlorobenzene	0.300	----
Chloromethane	0.100	----
1,1-Dichloroethane	0.100	----
1,1,2,2-Tetrachloroethene	0.300	----

[a] These compounds typically are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

1) **Chloromethane:** This compound is the most likely compound to be lost if the purge flow is too fast.

2) **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 line 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.

3) **Tetrachloroethane and 1,1-Dichloroethane:** These compounds are degraded by contaminated lines in the purge-and-trap systems and/or active sites in trapping materials.

Table 4. Recommended Gas Chromatographic Conditions.

Capillary Columns:	
Carrier Gas:	Helium
Flow Rate[1]:	10-15 mL/minute
Make-up Gas Flow[1]:	15-20 mL/minute
Initial Temperature:	35°C
Initial Hold Time:	1.0 to 5.0 minutes
Ramp Rate:	9°C/minute

Final Temperature: Final Hold Time:	210°C Until all target compounds elute

[1]Flow rates described here are those designed to be used with a jet separator. The total flow rate into the jet separator is generally 25 to 30 mL/minute, depending on the manufacturer's specifications.

Table 5. Recommended Purge-and-Trap Analytical Conditions.

Purge Conditions:	
Purge Gas:	Helium
Purge Time:	11.0 minutes
Purge Flow Rate:	35 - 40 mL/minute
Purge Temperature:	Ambient (water), required 40°C (low level soil)
Desorb Conditions[a]:	
Desorb Temperature:	180/250°C
Desorb Time:	2.0 minutes
Bake Conditions:	
Bake Temperature:	180/260°C
Bake Time:	8.0 minutes

[a]Desorb and trap conditions may vary depending upon trap adsorbents used.

Table 6. Required Mass Spectrometer Analytical Conditions.

Electron Energy	70 volts (nominal)
Mass Range	35-300 amu
Scan Time	To give at least 5 scans per peak, not to exceed 1 second per scan for capillary column To give at least 5 scans per peak, not to exceed 2 seconds per scan for packed columns
Transfer Line Temperature	Hewlett-Packard - 150°C
Source Temperature	Hewlett-Packard - 130°C

Table 7. Method 8260 Volatile Internal Standards With Corresponding Target Compounds and System Monitoring Compounds Assigned For Quantitation.

Fluorobenzene	**Chlorobenzene-d_5**	**1,4-Dichlorobenzene-d_4**
1,1,1-Trichloroethane	1,1,1,2-Tetrachloroethane	1,2,3-Trichlorobenzene
1,1,2-Trichloroethane	1,1,2,2-Tetrachloroethane	1,2,4-Trichlorobenzene
1,1-Dichloroethane	1,2,3-Trichloropropane	1,2-Dibromo-3-chloropropane (DBCP)
1,1-Dichloroethene	1,3-Dichlorobenzene	1,2-Dichlorobenzene
1,1-Dichloropropene	1,2,4-Trimethylbenzene	1,4-Dichlorobenzene
1,2-Dichloroethane	1,3,5-Trimethylbenzene	Hexachlorobutadiene
1,2-Dichloropropane	2-Chlorotoluene	n-Butylbenzene
1,2-Dibromoethane (EDB)	4-Bromofluorobenzene(smc)	Naphthalene

Fluorobenzene	Chlorobenzene-d_5	1,4-Dichlorobenzene-d_4
1,3-Dichloropropane	4-Chlorotoluene	p-Isopropytoluene
1,4-Dioxane	Bromobenzene	trans-1,4-Dichloro-2-butene
2-Butanone	Bromoform	
2,2-Dichloropropane	Chlorobenzene	
2-Hexanone	Ethylbenzene	
4-Methyl-2-pentanone	Isopropylbenzene	
Acetone	m,p-Xylene	
Acetonitrile	n-Propylbenzene	
Acrolein	o-Xylene	
Acrylonitrile	sec-Butylbenzene	
Benzene	Styrene	
Benzyl Chloride	tert-Butylbenzene	
Bromochloromethane	Tetrachloroethene	
Bromodichloromethane	Toluene-d_8 (smc)	
Bromomethane	Xylene (total)	
Carbon disulfide	Methacrylonitrile	
Carbon tetrachloride	Propionitrile	
Chloroethane	1-Chlorohexane	
Chloroform		
Chloromethane		
Chloroprene		
cis-1,2-Dichloroethene		
cis-1,3-Dichloropropene		
Dibromochloromethane		
Dibromfluoromethane (smc)		
Dibromomethane		
Dichlorodifluormethane		
Ethyl Methacrylate		
Iodomethane		
Isobutyl Alcohol		
Methacrylonitrile		
Methylene Chloride		
Methyl Methacrylate		
Propionitrile		
Tetrachloroethene		
Toluene		
Toluene-d8 (smc)		
Trichloroethene		
trans-1,2-Dichloroethene		
trans-1,3-Dichloropropene		
Trichlorofluoromethane		
Vinyl Acetate		
Methyl-tert-butyl ether		
1,1,2-Trichloro-1,2,2-trifluoroethane		

(smc) = system monitoring compound.

Appendix A

Variations to this SOP for AFCEE 3.0 Analysis

Since the AFCEE QAPP 3.0 is very specific, all information available in the QAPP will not be repeated in this SOP. Anyone dealing with AFCEE should have a copy of the QAPP and be familiar with its contents. The AFCEE QAPP is located in the GC/MS laboratory. Additional project instructions can be located in the PEL company folder to which each analyst has access.

1. ALL SAMPLES MUST BE LOGGED OUT OF THE INTERNAL CHAIN-OF-CUSTODY BOOK UPON REMOVAL FROM LOGIN AND LOGGED BACK IN UPON RETURN TO THE SECURED VOLATILES REFRIGERATOR.

2. Calibration

a) Initial calibration criteria listed in this SOP is valid. Three additional options are also provided in the AFCEE QAPP, but PEL Laboratories only utilizes the following two:
   i) Curve must have mean ≤ 15% RSD for all analytes. With no single analyte >30%.
   ii) Linear – least squared regression, r > 0.995
b) The calibration curve for AFCEE analysis requires additional standards. The concentrations and standard volumes required may be found in the back cover of each instrument book.
c) A second vendor standard is analyzed immediately following the calibration curve and must be ≤ 25% difference.
d) Lowest point of initial calibration must be at or below AFCEE report limits. Several compounds require lower calibration points than others to meet these reporting limits. In the initial curve, each compounds low calibration point will be reflected. However if a compound has a higher low calibration point than another, the lower points will be disabled in the Target software. For example, Bromoform requires a 2µg/L low calibration point, which is higher than other compounds (some require a 0.5µg/L point). The lower points will be disabled in the Target software to reflect this requirement for Bromoform.
e) All calibration analytes must be within +/- 20% of expected value-no averaging permitted.
f) Internal standard requires retention time +/- 30 seconds from retention time of the mid-point on the initial calibration. (The software currently references from our last CCV utilized.)

3. Surrogates
   g) Acceptability is not based on laboratory-established limits.
   h) Acceptance limits for waters and soils are listed in AFCEE QAPP.

4. Spikes
   i) MDL must be less than or equal to one-half of AFCEE reporting limit.
   j) Matrix spike and matrix spike duplicates (MS/MSD) will be prepared as requested by project.
   k) Acceptability is not based on laboratory-established limits.
   l) Quality Control Acceptance limits for waters and soils are listed in AFCEE QAPP.
   m) Because the MS/MSD are included in the batch only 18 field samples may be analyzed in an AFCEE batch.

5. Data Reduction/Reporting
   n) AFCEE reporting limits are listed in the AFCEE QAPP and are different from PEL Laboratories standard reporting limits.
   o) Associated internal standards for analytes are listed in the AFCEE QAPP.
   p) Data are qualified to the MDL based on instructions in AFCEE QAPP.
   q) Significant figure rules do not apply. AFCEE requires that MDLs and results are reported to one more decimal place than AFCEE reporting limit, without regard to significant digits.
   r) MDLs and report limits are not corrected for dry weight or dilution on the Form O-2, however initial weights extracted are raised based on percent solids.
   s) Qualifiers are applied to results based on instructions in AFCEE QAPP.
   t) AFCEE deliverables are designated in AFCEE QAPP.
   u) The necessity for manual integration and the circumstances involved are discussed in the appropriate PEL SOP.

6. Corrective action is identified in the AFCEE QAPP.

PEL Laboratories, Inc.

PEL Laboratories, INC. - Standard Operating Procedure

Sample analysis: cations by ICP (EPA 200.7, 6010B, AFCEE 3.0, and CLP ILM 4.0)

APPROVED:

Trace Metals Team Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL laboratories, Inc.. to analyze aqueous and solid sample digestates for selected cations (metals, also referred to as elements in this document) by using inductively coupled plasma atomic emission spectroscopy (ICP/AES or ICP). Table 1 lists the elements that can be analyzed using this SOP along with their analytical wavelengths and working linear ranges.

This standard operating procedure can be used for the following applications.

1. Dissolved elements determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L.
2. Total element determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects.

This SOP presupposes that the analyst has working knowledge and experience in the operation of ICP equipment and data system. Analysts performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. The area team leader or section leader is responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

INTERFERENCES

Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the element line.

The actual Inter-Element Correction (IEC) factor is calculated by running a single element standard of the suspected interfering element at a high (10-500mg/L) concentration; any concentration in the other metals > the reporting limit is corrected. This correction factor is entered into the computer, and is used to correct for interferences that occur during the run.

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, using a peristaltic pump, the addition of an internal standard, or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift.
Chemical interferences Include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (Incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific element.

The TJA Trace Analyzer utilizes an Internal Standard (Yttrium) to help correct for physical interferences. During both calibration and analysis, this reference element is measured at an independent wavelength, and all analyte emission intensities are divided by the reference line intensity to calculate an *intensity ratio*. This intensity ratio can be calculated using either gross emission or background corrected emission intensities. Calibration curves are then fit to intensity ratio values taken from the standards, and intensity ratios taken from the samples are used to interpolate analyte concentrations on the calibration curves.

ANALYSIS RATE

Up to 150 field samples can be analyzed sequentially by the TJA Trace Analyzer.

QA/QC REQUIREMENTS

The holding time for this test is 180 days from sampling to final analysis.

This SOP was written to conform to all QA/QC criteria described in the following methods: EPA 200.7, SW-846 6010B, CLP ILM 4.0, and AFCEE 3.0. Listed methods are valid for aqueous samples and non-aqueous samples.

Initially the following requirements must be met.

MDLs (must be repeated every 12 months) - A minimum of seven samples are prepared at a concentration between 1-10 times the expected MDL. The samples are analyzed within a valid analytical sequence. The validated detection limit is calculated by multiplying the standard deviation of the replicate results by 3.143, which is the one-sided Student's t value for a 99% confidence interval and 6 degrees of freedom. Reporting limits are valid only if they are greater than or equal to the validated method detection limit values. Standard reporting limits can be any convenient value that meets the above criterion. However, the reporting limit for each target must be reconsidered for every sample by reviewing the maximum contaminant level for each element.

Four replicates - Method performance validation is performed by analyzing at least four replicate spiked water samples. To establish initial method precision and accuracy, calculate mean % recovery and percent relative standard deviation (RSD) of each target compound.

Tables 2-8 list the ICP standards used by PEL Laboratories, Inc., and how each standard is prepared. All ICP standards are prepared in a 6% HNO_3 + 5% HCl matrix.

Table 9 lists an example analytical sequence, and quality control criteria for the following: initial calibration verification (ICV), initial calibration blank (ICB), interference check solution A (ICSA), interference check solution A and B (ICSAB), method blank (MB), Laboratory control sample (LCS), matrix spike (MS), matrix spike duplicate (MSD), serial dilution (SD), post-digestion spike (PDS), continuing calibration verification (CCV), and continuing calibration blank (CCB).

Samples must be prepared and analyzed as part of an analytical batch. An analytical batch is defined at the sample preparation step. However, multiple analytical batches can be analyzed on a single run. All criteria cited in Table 9 must also be followed for each subsequent preparatory batch analyzed.

At times it may be necessary to break a batch for analysis. This implies that some of the samples in the batch are analyzed during a different or non-continuous time interval as the others, or on a different instrument. In these cases, the method blank associated with that batch will be analyzed with the separated portions of the batch.

Linear range and IEC studies are checked and updated annually or whenever a significant change occurs in the instrument.

For Level III & IV, AFCEE, and ILM 4.0, a serial dilution shall be performed for each analytical batch.

Analytical Method used for analysis is documented on the cover page of raw data.

EQUIPMENT/APPARATUS

Inductively Coupled Plasma-Atomic Emission Spectrometer: TJA ICAP 61E Trace Analyzer with a dedicated personal computer running Thermo-Spec software.

REAGENTS

1. Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.
   a) Hydrochloric acid, concentrated specific gravity = 1.19 (HP Instra-Analyzed. CAT# 9530-33
   b) Nitric acid, concentrated specific gravity = 1.41 (HP Instra-Analyzed. CAT# 9598-34)
2. Reagent grade water. ASTM type II
3. Standards. Each standard must have a unique ID, and all standard preparation must be documented. All standards must be labeled with a unique ID, name of the standard, concentration, and expiration date. They are stored at room temperature on the bench or shelf. Most standards for ICP analysis are prepared using 6.0% HNO_3 and 5.0% HCL as the solvent. Standards for ICP analysis are stored in FEP fluorocarbon or polyethylene bottles.
   a) Single element standards purchased from High Purity Standards (HP) or equivalent vendor:
      i. Aluminum (1), 10,000 mg/L, High Purity, CAT# 10M1-1
      ii. Antimony, 1000mg/L, HP, CAT#10002-1.
      iii. Arsenic, 1000 mg/L, HP, CAT# 10003-1.
      iv. Barium, 1000mg/L, HP, CAT# 10004-1.
      v. Beryllium, 1000mg/L, HP, CAT# 10005-1.
      vi. Cadmium, 1000mg/L, HP, CAT# 10008-1.
      vii. Calcium, 10,000mg/L, HP, CAT# 10M9-1.
      viii. Chromium, 1000mg/L, HP, CAT# 100012-1.
      ix. Cobalt, 1000mg/L, HP, CAT# 100013-1.
      x. Copper, 1000mg/L, HP, CAT# 100014-1.
      xi. Iron, 10,000mg/L, HP, CAT# 10M26-1.
      xii. Lead, 1000mg/L, HP, CAT# 100028-1.
      xiii. Magnesium, 10,000mg/L, HP, CAT# 10M31-1.
      xiv. Manganese, 1000mg/L, HP, CAT# 100032-1.
      xv. Molybdenum, 1000mg/L, HP, CAT# 100034-1.
      xvi. Nickel, 1000mg/L, HP, CAT# 100036-1.
      xvii. Potassium, 1000mg/L, HP, CAT# 10M41-1.
      xviii. Selenium, 1000mg/L, HP, CAT# 100049-1.
      xix. Silver, 1000mg/L, HP, CAT#100051-1.
      xx. Sodium, 1000mg/L, HP, CAT# 10M52-1.
      xxi. Thallium, 1000mg/L, HP, CAT# 100058-1.
      xxii. Tin, 1000mg/L, HP, CAT# 100061-1.
      xxiii. Vanadium, 1000mg/L, HP, CAT# 100065-1.
      xxiv. Yttrium, 1000mg/L, HP, CAT# 100067-1.

xxv.Zinc, 1000mg/L, HP, CAT# 100068-1.

b) Mixed standard solutions. Prepare the three mixed standards according to Tables 2-4. Note that the first one of the standards listed is the initial calibration blank. The other standards are prepared according to the analysis that will be performed.
c) Initial calibration verification standards (ICV). Initial calibration is verified by analysis of mixed ICV solution shown in Table 5. Stock solutions:
   i. CPI Spiking solution #1 25 mg/L of Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Sn, V, Zn (CAT#4400-13085)
   ii. CPI Spiking solution #2 2500 mg/L of Al, Ca, Fe, Mg, K, Na.
d) Interference check standards (ICSA and ICSAB), are diluted from a purchased set. Tables 6 and 7 provide the composition of the interference check standard solutions.
   i. HP ICSA, 5,000 mg/L of Al, Ca, and Mg, and 2,000of Fe CAT# CLP-INF-1.
   ii. CPI Spiking solution #1 (see above for concentrations of elements and CAT#).
e) Continuing calibration verification standards (CCV). Is made by mixing equal parts of STD2 and STD3. Resulting concentrations are listed in Table 8.

PROCEDURE

1. Instrument start-up for TJA
   a) Verify that Argon supply is on (60 psi required supply pressure).
   b) Verify that the exhaust vent over plasma stack is on at all times.
   c) Turn on computer and printer.
   d) Verify that RF generator and water recirculator pump are on.
   e) Access "Thermo-Spec" software.
   f) Use arrow keys on main menu to access "Setup".
   g) Place cursor at "Plasma Control Panel" and press "Enter".
   h) Install new pump tubing on peristaltic pump and place nebulizer capillary tube in a clean rinse solution (as needed).
   i) Key the F1 function in the plasma control panel menu to initialize the plasma "Start" sequence. Follow the instructions provided.
   j) After plasma ignition, key F2 function to enter the "levels" page. Set nebulizer pressure to 28 psi, RF power to 950 watts, and peristaltic pump rate to 130 RPM.
   k) After a 60-minute warm-up period, profile the instrument with a 5 ppm arsenic standard, and adjust micrometer as necessary.
2. After the instrument has become thermally stable and profiled, initiate appropriate operating configuration of computer by following manufacturers recommendations.
3. Analyze the initial calibration standards according to the sequence listed in Table 9 and flush the system with the calibration blank between each standard.
4. Begin the sample run:
   a) At minimum, duplicate exposures are required for all analytical runs. The average result of the multiple exposures for the standards and all QC and sample analyses is used.
   b) Set up an analytical sequence. In the "Methods" section of the software, for the TJA. Calibration standards, QC samples and field samples must be analyzed in a pre-determined sequence in order to be valid (see Table 9).
5. QC criteria must be monitored on a real-time basis, and all criteria must be met in order to complete the analytical sequence. If any QC sample does not meet criteria, stop the analytical sequence and perform corrective action.

CALCULATIONS

Equation 1. Calculation of cations concentration in aqueous samples.

$$Concentration\,(ppb\ or\ \mu g/L) = Concentration\ of\ digestate\,(\mu g/L) \times Dilution\ factor$$

Equation 2. Calculation of cations concentration in solid samples, adjusted to dry weight.

$$Concentration\,(ppm\ or\ mg/Kg) = \frac{Concentration\ of\ digestate\,(mg/L) \times Volume\ of\ digestate\,(L) \times Dilution\ factor}{Weight\ of\ sample\,(Kg) \times \left(Percent\ Solids / 100\right)}$$

Equation 3. Calculation of matrix spike recoveries.

$$\%R = \frac{Spiked\ sample\ result\ -\ Native\ sample\ results}{Spike\ amount\ added} \times 100$$

Equation 4. Calculation of blank spike or LCS recoveries.

$$\%R = \frac{Blank\ spike\ result}{Spike\ amount\ added} \times 100$$

Equation 5. Calculation of relative percent difference.

$$RPD = \frac{|Replicate\ 1 - Replicate\ 2|}{Replicate\ 1 + Replicate\ 2} \times 200$$

DOCUMENTATION

Unique standard IDs must be documented in a run log or cover sheet. Standard preparation date must also be Included.

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to the team/section leader and/or the safety officer.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

- *Method for the Determination of Metals in Environmental Samples,* U.S.EPA 600-4/91/010, Method 200.7
- *Test Methods for Evaluating Solid Waste,* EPA SW-846 Method 6010B and Chapter 3 – "Metallic Analytes"

Table 1. ICP elements, wavelength, linear range

Element	Wavelength, nm	RL* (µg/L)	URL[ab] (µg/L)
Aluminum	308.215	50	1,000,000
Antimony	206.838	5	25,000
Arsenic	189.042	5	25,000
Barium	493.409	1	5,000
Beryllium	313.042	1	5,000
Cadmium	226.502	1	10,000
Calcium	315.887	100	1,000,000
Chromium	267.716	1	25,000
Cobalt	228.616	1	25,000
Copper	324.754	2	20,000
Iron	271.441	50	400,000
Lead	220.353	2	25,000
Magnesium	279.079	50	1,000,000
Manganese	257.610	2	20,000
Molybdenum	202.030	2	10,000
Nickel	231.604	2	25,000
Potassium	766.491	100	200,000
Selenium	196.026	5	20,000
Silver	328.068	1	1,000
Sodium	330.237	200	1,000,00
Tin	189.989	6	25,000
Thallium	190.864	6	20,000
Vanadium	292.402	1	25,000
Zinc.	213.856	10	10,000

* RLs are project specific for AFCEE and Level III & IV work. The RLs listed in this table are for the level I and II work performed by PEL.

a) If the concentration of an element is above the URL, it must be diluted until the value is below the URL and this concentration should be reported.

b) If the concentration of an interfering element is above the URL, the sample should be diluted until the value of this element is below the URL, and the diluted values for any elements affected by this interfering element. The adjusted RL should be reported, noting matrix interference. For AFCEE and level III work, a formal communication must be sent to the client if an RL is raised, **AND** a non-detect is reported.

Table 2. Calibration Blank (STD1-BLANK)*

Standard Name	Volume of Stock	Final Volume	Final Concentration (mg/L)
STD1-BLANK	30 mL HNO_3 + 25 mL of HCl	500mL	0. 0

*Also used as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

Table 3. Calibration Standard #2 (STD2)

Standard Name	Volume of Stock	Final Volume	Final Concentration (ug/L)
STD2	50.0 mL of CLP-INF-1 (5,000mg/L Ca, Mg, Al, and 2,000mg/L Fe) 25ml of a 10,000mg/L standard for Na and K.	1000	250,000ug/L of Ca, Mg, Al, Na, K, and 100,000ug/L of Fe

Table 4. Calibration Standard #3 (STD3)

Standard Name	Volume of Stock	Final Volume	Final Concentration (ug/L)
STD3	25mL of a 25mg/L standard for Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V, Zn	1000mL	1,000ug/L for metals listed to left

Table 5. Initial Calibration Verification (ICV)

Standard Name	Volume of Stock	Final Volume	Final Concentration (ug/L)
ICV	10 mL of CPI Spike #1	500mL	500ug/L for metals listed in stock
	10 mL of CPI Spike #2	500mL	50,000ug/L for metals listed in stock

Table 6. Inter-element Correction Solution-A (ICSA)

Standard Name	Volume of Stock	Final Volume	Final Concentration (ug/L)
ICSA	50.0 mL of CLP-INF-1 (5,000mg/L Ca, Mg, Al, and 2,000mg/L Fe)	500	500,000ug/L of Ca, Mg, Al and 200,000ug/L of Fe

Table 7. Inter-element Correction Solution-A+B (ICSAB)

Standard Name	Volume of Stock	Final Volume	Final Concentration (ug/L)
ICSAB*	50.0 mL of CLP-INF-1 (5,000mg/L Ca, Mg, Al, and 2,000mg/L Fe)	500mL	500,000ug/L of Ca, Mg, Al and 200,000ug/L of Fe
	10 mL of CPI Spike #2	500mL	500ug/L for metals listed in stock

*Note: Please refer to ILM 4.0 for CLP specific analyte concentrations.

Table 8. Continuing Calibration Verification (CCV)

Standard Name	Volume of Solution	Final Volume	Final Concentration (ug/L)
CCV	500mL of STD2 + 500mL of STD3	1000mL	500ug/L for Ag, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V, Zn
			125,000ug/L for Al, Ca, Mg, K, Na
			50,000ug/L for Fe

Table 9. Analytical sequence and QC requirements for ICP analysis[‡]

Analysis	Description	EPA 200.7	SW-846 6010B and AFCEE	CLP ILM 4.0
Initial calibration sequence				
		Select appropriate standards from Table 5 according to the elements to be determined.		
ICB	Initial calibration blank			
STD3	Initial calibration standard 3			
STD2	Initial calibration standard 2			
ICV	Initial calibration verification standard	95-105%	90-110%	90-110%
ICB	Initial calibration blank	≤ RL	≤RL	< RL
ICSA	Interference check sample, mix A	Test at beginning.[a]	Test at beginning.[a]	Test at beginning.[a]
ICSAB	Interference check sample, mix AB	80-120%, test at beginning.[a]	80-120%, test at beginning.[a]	80-120%, test at beginning.[a]
	Sample analysis			
MB	Method blank	≤MDL[b]	< RL[b]	< RL
LCS	Laboratory control sample	80-120%[c]	80-120%[c]	80-120%[c]
S1	Sample 1 native			
S1MS	Sample 1 matrix spike	75-125%[c]	75-125%[c] or per project instructions	75-125%[c]
S1MSD	Sample 1 matrix spike duplicate	75-125%[c] rec. ≤ 20% RPD	75-125%[c] rec. ≤ 20% RPD[c] or per project instructions	75-125%[c] rec. ≤ 20% RPD
S1PDS	Sample 1 post-digestion spike	75-125%[c]	[c]75 – 125%[c] For AFCEE, perform only if serial dilution fails criteria	N/A
S1SD	Sample 1 serial dilution	1:5 dilution ± 10%, perform only if matrix effect is suspected	1:5 dilution. Diluted result must agree within ± 10% of undiluted result if native result is >50x the MDL.	1:5 dilution. Diluted result must agree within ± 10% of undiluted result if native result is >50x the MDL.
S2	Sample 2			
S3	Sample 3			
CCV	Continuing calibration check standard	95-105%[d]	90-110%[d]	90-110%[d]
CCB	Calibration blank	< RL[d]	< RL[d]	< RL[d]
S4	Sample 4			
S5	Sample 5			
S6	Sample 6			
S7	Sample 7			
S8	Sample 8			
S9	Sample 9			
S10	Sample10			
S11	Sample 11			
S12	Sample 12			

Analysis	Description	EPA 200.7	SW-846 6010B and AFCEE	CLP ILM 4.0
S13	Sample 13			
CCV	Continuing calibration check standard	95-105%[d]	90-110%[d]	90-110%[d]
CCB	Calibration blank	< RL[d]	< RL[d]	< RL[d]
S14	Sample 14			
S15	Sample 15			
S16	Sample 16			
S17	Sample 17			
S18	Sample 18			
S19	Sample 19			
S20	Sample 20			
S21	Sample 17			
S22	Sample 18			
S23	Sample 19			
CCV	Continuing calibration check standard	95-105%[d]	90-110%[d]	90-110%[d]
CCB	Calibration blank	< RL[d]	< RL[d]	< RL[d]

[‡] Flush the system with calibration blank solution between each analytical run for at least 60 seconds. This rinse time can be Increased or decreased based the expected levels of the analytes of interest.

Corrective actions:

[a] **If criteria are not met, terminate run, correct the problem and recalibrate the instrument. See Table 10 for acceptance criteria.**

[b] If the method blank fails the stated criteria, the associated samples may require re-preparation and reanalysis unless the following criteria is met: *if the blank concentration is above the RL, the lowest concentration in the associated samples may not be less than 10x the blank concentration. If the lowest concentration is less than 10x the blank concentration or if the concentration of the blank is less than negative RL, re-prepare and re-analyze the samples.*

[c] See Table 11 for LCS, MS, and MSD spiking levels.

[d] If the CCV or CCB are outside stated criteria for the applicable method, recalibrate and reanalyze all samples from the previous acceptable CCV and CCB.

Table10. ICS Acceptance Criteria

Element	ICSA	ICSAB
Silver	+/- 3ppb	80-120%
Aluminum	80-120%	80-120%
Arsenic	+/- 6ppb	80-120%
Barium	+/- 3ppb	80-120%
Beryllium	+/- 3ppb	80-120%
Calcium	80-120%	80-120%
Cadmium	+/- 3ppb	80-120%
Cobalt	+/- 3ppb	80-120%
Chromium	+/- 3ppb	80-120%
Copper	+/- 6ppb	80-120%
Iron	80-120%	80-120%
Potassium	+/- 300ppb	80-120%
Magnesium	80-120%	80-120%
Manganese	+/- 3ppb	80-120%
Molybdenum	+/- 6ppb	80-120%
Sodium	+/- 600ppb	80-120%
Nickel	+/- 6ppb	80-120%
Lead	+/- 6ppb	80-120%
Antimony	+/- 6ppb	80-120%
Selenium	+/- 9ppb	80-120%
Tin	+/- 9ppb	80-120%
Thallium	+/- 18ppb	80-120%
Vanadium	+/- 3ppb	80-120%
Zinc.	+/- 30ppb	80-120%

Note: For Level III & IV, AFCEE 3.0, and CLP ILM 4.0, the ICSA criteria will be based on client specific reporting limits.

Table 11. Spiking levels for LCS and matrix spikes.

Element	Spiking level (µg/L)
Aluminum	50,000
Antimony	500
Arsenic	500
Barium	500
Beryllium	500
Cadmium	500
Calcium	50,000
Chromium	500
Cobalt	500
Copper	500
Iron	50,000
Lead	500
Magnesium	50,000
Manganese	500
Molybdenum	500
Nickel	500
Potassium	50,000
Selenium	500
Silver	500
Sodium	50,000
Thallium	500
Tin	500
Vanadium	500
Zinc.	500

PEL Laboratory - Standard Operating Procedure

Sample Analysis for Chlorophenoxy Acid Herbicides by Capillary Gas Chromatography (SW-846 8151A)

APPROVED:

Section Supervisor Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL laboratory to determine the concentrations of various chlorophenoxy acid herbicides in extracts from a variety of matrices using method 8151. Open-tubular, capillary columns are used with electron capture detectors (ECD).

Although many compounds can be determined using SW 846 method 8151, it is the intention of the laboratory to report a standard target list. Additional compounds may be reported as identified by specific project plans or client requests. According to SW 846 method 8151, it is unlikely that all of the targets listed in the method could be determined in a single analysis. This limitation results because the chemical and chromatographic behavior of many of these chemicals can result in co-elution. Any chemical is a potential method interferent when it is not a target analyte.

A measured volume or weight of sample (approximately 1 L for aqueous samples, 30 g for solids) is extracted using the appropriate sample extraction technique. Report limits are adjusted accordingly for less than normal extraction aliquots. Liquid samples are extracted at neutral pH with ethyl ether using separatory funnel (SW846 method 3510). The acids are converted to their methyl esters using diazomethane as a derivitizing agent. There is a final solvent exchange to MTBE (see PEL extraction SOPs for comprehensive a review of sample preparation).

The extract is analyzed by injecting 1μL of sample into a gas chromatograph with fused silica capillary columns and electron capture detectors. All chromatographic data are acquired onto a centralized computer for convenient post-run processing, review, workup, and archival. Chemical components are qualitatively identified by absolute retention times on dissimilar analytical columns and quantified by relative response factors, both values being calculated relative to internal standard, 4,4'-dibromoctafluorobiphenyl. Multi-level calibration is performed prior to sample analysis.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

Compounds which may be determined using this SOP are listed below. Analysis will be performed in accordance with this SOP for method 8151.

ANALYTE	CAS#
Dalapon	75-99-0
Dicamba	1918-00-9
MCPP	93-65-2
MCPA	94-74-6
Dichloroprop	120-36-5
2-4-D	94-75-7

2,4,5-TP (Silvex)	93-72-1
2,,4,5-T	93-76-5
4,4'-DDT	50-29-3
2,4-DB	94-82-6
Dinoseb	88-85-7
Picloram	1918-02-1
Bentazon	25057-89-0
4-Nitrophenol	100-02-7
Pentachlorophenol	87-86-5

For current method detection limits refer to the latest version of the PEL quality manual.

Appendix A outlines differences from this SOP for AFCEE 3.0 analysis.

QA/QC REQUIREMENTS

The holding time for this test is 40 days after extraction.

Target compounds tentatively identified in unfamiliar samples require confirmation by at least one additional qualitative technique.

Initially the following requirements must be met.

1. Method Detection Limit Study (MDLs) - A minimum of seven samples are prepared, each at a concentration equal to or near the current report limit. The samples are analyzed within valid analytical sequence. The validated detection limit is calculated by multiplying the standard deviation of the replicate results by 3.14, which is the one-sided Student's t value for a 99% confidence interval and 6 degrees of freedom. Reporting limits are valid only if they are greater than or equal to the validated method detection limit values. Standard reporting limits can be any convenient value that meets the above criterion, but are typically equal to the lowest calibration level. However, the report limit for each target must be reconsidered for every sample by viewing the chromatogram and associated quantitation report. MDLs will be repeated every 12 months.
2. Precision and Accuracy (four replicates) – An initial demonstration of precision and accuracy must be performed by new analysts. Method performance validation is performed by analyzing at least four replicates of spiked water samples. To establish initial method precision and accuracy, calculate mean % recovery and percent relative standard deviation (RSD) of each target compound. The average recovery and RSD of the four replicates must be within the range provided by the respective analytical method.
3. Demonstration of adequate target peak resolution.
4. Demonstration of adequate instrument sensitivity through analysis of standards at or below reporting limits.
5. Demonstration of validity of calibration standards through analysis of QC reference standard. The analyst will analyze a QC reference standard (prepared from a second source standard).

The following procedures will be used to demonstrate that the system is in control on an on-going basis. Applicable ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

6. Blanks
    A. A calibration blank, (MTBE goes through the extraction process with the standards) is analyzed with each calibration performed and is used to check for interferences that may have been introduced in the preparation of standards. The analyst will analyze an instrument blank to demonstrate that interference from the analytical system are under control during initial calibration.
    B. The method blank is processed through the same extraction, concentration, and cleanup procedures as the samples and can have no targets above the report limit. Laboratory blank water and Ottawa sand will be used as the matrix for method blanks. A method blank is prepared with every prep batch or every twenty samples whichever is more frequent.

C. Trip, equipment, and field blanks are provided by the client to monitor contamination during sampling and shipping. These types of blanks are treated as regular samples by the laboratory.

7. Surrogates - Surrogate is added to all samples (including QC samples) immediately before extraction to monitor the efficiency of each sample preparation. Poor surrogate recovery requires investigation. Re-extraction is the logical corrective action if sufficient raw sample is available and if the holding time has not expired. The surrogate compound is 2,4-dichlorphenyl acetic acid (DCAA). Acceptance limits are set at 60 – 130 percent until they can be determined from historical data..

8. Matrix spike/Matrix spike duplicate (MS/MSD) - an aliquot of an environmental sample is spiked with known quantities of the method analytes. The analytes spiked are dependent on project specifications. If no spiking requirements are communicated, spiking will be performed as specified in method 3500. The MS/MSD is analyzed exactly like a sample, and its purpose is to determine whether sample matrix contributes bias to the analytical results by determining the accuracy of each and the precision associated with the spikes. The background concentrations of the analytes in the native sample must be determined in a separate aliquot and the measured values in the MS/MSD corrected for native concentration. If the client has not identified samples to be spiked, the laboratory will randomly choose non-QC samples for spiking. MS/MSD results will be compared to established laboratory limits for acceptability. Since the native matrix may have a detrimental effect on accuracy and precision, a LCS is prepared with every MS/MSD. If MS/MSD does not meet acceptance criteria and the associated LCS is acceptable, matrix effect is assumed.

9. LCS (Blank spike) - Representative target compounds are spiked into a blank matrix (laboratory blank water or Ottawa sand). The LCS is processed through the same extraction, concentration, and cleanup procedures as the samples.

10. Internal standard - Internal standards are chosen that are similar in analytical behavior to compounds of interest. The internal standard should not be affected by normal method or matrix interference, and should offer large detector response which will serve to minimize the effects of compound coelution. Internal standard area should be within acceptance limits. The internal standard compound is 4,4'dibromooctafluorobiphenyl.

11. Instrument Performance - Significant peak tailing of the target compounds should be corrected. Tailing problems are generally traceable to active sites in the GC inlet, on the GC column, improper column installation, or problems with the operation of the detector.

12. Initial Calibration – a series of standards will be analyzed before sample analysis. The initial calibration will demonstrate:

    A. Linearity

    B. Sensitivity

    C. Deactivation of the analytical system

    D. Expected retention time of target analytes

13. Continuing calibration verification (CCV) – Standards will be analyzed every 12 hours to demonstrate that the initial calibration is still valid and that the analytical instrument is in control.

When any of the above criteria is not achieved, the analyst must repeat the test only for that analyte which failed to meet criteria. Repeated failure however will indicate a general problem with the measurement system or faulty samples and/or standards. If this occurs, locate and correct the source of the problem and repeat the test.

EQUIPMENT/APPARATUS

1. Microsyringes – 10uL, 25uL, and 100µL
2. Pipets
3. GC Vials
4. Syringes
5. Volumetric flasks
6. Centrifuge

7. A Hewlett Packard series II 5890 gas chromatograph equipped with split/splitless capillary injector and HP 7673 autosamplers. The instruments capable of chlorophenoxy acid herbicide analysis are also equipped with linearized dual electron capture detector(s).
8. Data System - In addition to data handling capabilities, the computerized data system offers varying degrees for instrument control. Data handling can be a major source of error in chromatographic analysis. Currently, the GC's are equipped with an HP 486/66XM computer with HP EnviroQuant and Target software for data processing.
9. GC Analytical Columns - The capillary columns currently used are a primary column, XTI-5 (Restek part #12240) and a confirmation column, RTX- 1701 (Restek part #12040) . Currently these columns are configured so that samples are injected onto both columns in order to acquire primary and confirmation data simultaneously. A press-tight "Y" quartz capillary column splitter connects both columns via a phenyl-methyl deactivated 0.5m, 0.53mm i.d. capillary quard column (Restek part #10045) mounted to the rear injector of the GC with each tail installed into a separate ECD. Reagents

1. Hexane – Pesticide grade, Burdick and Jackson Brand (catalog #216-4).
2. MTBE – Ultra Resi-Analyzed, Baker (catalog #9043-03).

Stock Standard Solutions – certified standard mixes may be purchased or mixes may be prepared by the laboratory. Stock Standards: The primary stock standard for herbicides is purchased from Accustandard. Catalog number M-8150A, underivatized chlorinated herbicides at 100ug/ml in methanol with MCPA and MCPP at 10000μg/ml is used.

Stock Surrogate Solution: Ultra Scientific 2,4-dichlorophenyl, acetic acid. Mix at 100μg/ml in acetone, catalog number PPS160.

Stock Internal Standard: Ultra Scientific 4,4'dibromooctafluorobiphenyl Mix at 100ug/ml in MTBE, catalog number PPS-170.

Spiking solutions are usually prepared in MTBE at a level of 0.10μg/ml for the herbicide mix and surrogate.

The secondary stock standard for herbicides is purchased from Accustandard. It is at 100μg/ml with MCPA and MCPP at 10,000 ug/ml in methanol.

3. Working Standard Solutions – prepared by dilution of stock standard solutions.

INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. Method blanks are prepared with field samples to demonstrate reagents and glassware are free of interference. Instrument blanks may be used to assess the level of interference produced by the GC instrument itself.

Sources of interference in this SOP can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of coeluting compound in the sample matrix to which the ECD will respond. Matrix interference may be caused by contaminants that are coextracted from the sample. The extent of matrix interference will vary considerably from source to source. Several cleanup procedures are used to minimize interferences coextracted from samples. Matrix interferences may be reduced or eliminated by Florisil cartridge cleanup procedures. Several of the pesticides will also recover from the sulfuric acid partitioning cleanup. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches.

Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. Common flexible plastics contain varying amounts of phthalate esters, which 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. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for phthalate contamination.

Glassware must be scrupulously cleaned.

PROCEDURE

1. Sample Extraction - See applicable extraction SOPs.
   a) Water samples may be prepared using method 3510 (separatory funnel) for extraction
   b) Soil, sediment and other solid samples may be prepared using method 3540 (soxhlet) or method 3550 (sonication) for extraction.
   c) Oils may be prepared using method 3580 (waste dilution) for preparation.
2. Retention Time Windows
   a) Retention time windows are based upon actual retention times of standards measured over the course of 72 hours.
   b) Retention time windows are defined as plus of minus three times the standard deviation of the absolute retention time for each standard.
   c) The experience of the analyst should weigh heavily in the interpretation of the pesticide chromatograms.
   d) For multi-component parameters, the analyst should use the retention time window but should primarily rely on pattern recognition.
3. Screening
   a) Extracts may be screened off-the-record prior to sample analysis.
   b) Screening allows for early recognition of surrogate and/or spike recovery problems, and potential interference thus initiating corrective action earlier.
   c) Dilutions can be predicted thus preventing instrument contamination/carryover or chromatographic damage on the calibrated instrument.
   d) Minimal screening calibration will be analyzed as deemed necessary by the analyst in order to accomplish screening objectives.
   e) Results will not be reported based on screening data.
4. Initial Calibration (appendix A lists typical initial calibration sequence of injections)
   a) Instrument blank should be analyzed to demonstrate that the analytical system is free of interference. No target should be detected above the report limit.
   b) Single-component herbicides may be combined in a single mix if all compounds in the mix are adequately resolved in all calibration levels. Method 8151 does not specify any resolution criteria. At a minimum, resolution between peaks should be 20%, although better resolution is recommended. Any compounds not adequately resolved should be analyzed in a separate mixture.
   c) No limit has been placed upon the amount of time that an initial calibration may be valid, nor is there a maximum limit on the number of samples associated with one initial calibration. As long as continuing calibration check standards meet criteria, then the initial calibration remains valid and samples may be analyzed.
   d) At a minimum the initial calibration will contain the following injections (order may vary, as long as analysis is completed before sample analysis).
   e) Acceptable calibration curves must be averaged to ≤ 20% RSD for all analytes, with no anlytes exceedin an RSD of 30%..

Initial Calibration Parameter	Acceptance Criteria
Minimum of five levels of single-response herbicides and surrogates. The low point should be equal to or below the report limit.	Coefficient of determination ≥ 0.995 or RSD ≤ 20%.
Instrument blank	No targets above report limit

5. Continuing Calibration Verification (CCV) - appendix B shows typical analytical sequence following initial calibration
   a) The validity of the herbicide initial calibration (primary curve) is verified by analyzing the calibration standard at a mid-level not less than every ten samples, and at the end of sample analysis for AFCEE work. The analyst may also analyze the CCV standards at higher and lower concentrations.
   b) The acceptance criteria is ± 15 percent difference from the expected value.
   c) Peak retention times should be within established retention time windows.
   d) Retention time windows may be recentered once per day. The updated retention time window will be calculated as the CCV retention time ± three times the standard deviation previously determined.

e) When any of the above criteria are is exceeded, inspect the gas chromatographic system to determine the cause and perform whatever maintenance is necessary before verify calibration and proceeding with sample analysis. If acceptable criteria are not met after instrument maintenance, a new initial calibration must be performed.

f) Internal standard (I.S.) - Whenever quantitation is accomplished using an internal standard, internal standard area must be evaluated for acceptance. The measured area of the internal standard must be no more or less than 50 percent different from the average area calculated during initial calibration (initial calibration average internal standard area ± 50%). When the internal standard peak area is outside the limit, all affected samples should be reanalyzed.

6. Sample Analysis

a) Sample analysis may continue for as long as the standard QC requirements are met.

a) If targets exceed the instrument calibration range, the extract must be diluted and reanalyzed. When sample extract is diluted to prevent one or more targets from exceeding instrument calibration range, all other report limits are adjusted according to dilution factor. Therefore the analyst tries to dilute so that targets are in the upper region of the curve.

b) Typically the analyst will analyze samples so that lowest report limits are achieved.

c) Frequently interferences will persist in the extract. Precise rules for diluting interferences are difficult to develop. A single non-target peak could be allowed to saturate the detector. But some extracts might elevate the baseline or alter the baseline noise for part of the chromatogram. Allowing the baseline to severely elevate or noise to obstruct the target chromatographic region would serve no purpose.

d) The results of all injections that follow a high level sample or a sample with late eluting compounds must be carefully examined for the possibility of crossover. Questionable samples should be reanalyzed.

e) Instrument blanks may be analyzed after suspect samples to evaluate instrument crossover. Such samples may be identified during screening.

f) Surrogate recovery is calculated for all samples, blanks, and spikes. Some samples will be diluted for analysis, diluting out the surrogates and therefore recovery cannot be determined. Calculated recoveries should be within laboratory generated recovery limits.

i) Two surrogate compounds are spiked. Decachlorobiphenyl is evaluated as the primary surrogate. If decachlorobiphenyl recovery is outside of acceptable limits, tetrachloro-m-xylene recovery should be compared to acceptance limits.

ii) If recoveries are not within acceptance limits, calculations should be verified. The surrogate spiking solution concentration, amount added, and actual concentration calculation should be evaluated for errors.

iii) High recoveries may be attributed to interfering peaks. Chromatograms will be examined for chromatographic interference. Recovery from both analytical columns may be evaluated.

iv) Familiar samples with a history of non-compliant surrogate recovery may not require further corrective action.

v) Analyst should determine if the problematic sample has a field duplicate or matrix spike/matrix spike duplicate. If non-compliant recovery is reproduced in a field duplicate or MS/MSD, the sample has already been extracted more than once and matrix effect may be assumed.

vi) Extraction logs should be examined for difficulties noted during sample preparation (i.e., emulsions).

vii) Extract may be reanalyzed to verify result.

viii) If investigation does not provide explanation, sample should be re-extracted if adequate sample volume is available.

g) Internal standard (I.S.) - Whenever quantitation is accomplished using an internal standard, internal standard area must be evaluated for acceptance. The measured area of the internal standard must be no more or less than 50 percent different from the average area calculated during initial calibration (initial calibration average internal standard area ± 50%). When the internal standard peak area is outside the limit, all samples that fall outside the QC criteria should be reanalyzed. Often high area is caused by coeluting peaks (matrix interference). Extract should be diluted and analyzed to minimize matrix effect. It should be noted that oily samples often suppress ECD baseline, lowering internal standard area, and further dilution may be required.

h) Single-component determination. Peak must be within established retention time window. Response must be within the instrument calibration range. If the response exceeds the instrument calibration range, sample must be diluted and analyzed.

7. Confirmation

a) Compounds tentatively identified (in unfamiliar samples) on one analytical column should be confirmed on a second, dissimilar analytical column (or should be supported by at least one other qualitative technique).

b) Calibration criteria for the confirmation column is the same as for the primary column. At a minimum, the criteria must only be met for the compound(s) being confirmed. For example, if Dalapon is not tentatively identified on the primary column, Dalapon does not have to meet initial and continuing calibration criteria on the confirmation column.
c) For positive hits, the result between the two analytical columns should be similar. If results vary significantly, the analyst should examine chromatographic data to see if one column may be inflated by coeluting peaks.

8. Data Reduction
   a) Chromatographic data should be reviewed as soon after acquisition as possible.
   b) Analyst should examine chromatogram for correct handling of baseline.
   c) The data system performs the first level of data reduction.
   d) The method algorithms should be established to bias for false positives.
   e) The analyst will review quantitation report against laboratory report limits.
   f) If any hit are tentatively identified on the primary column, the confirmation column results should be examined for confirmation of hits.
   g) Peak shape and pattern in samples should resemble applicable standards. Although some variation is expected due to weathering and fractionation.
   h) Determining that a compound is not confirmed based on second column is a form of quantitation and therefore the same criteria is used for both analytical columns.
   i) The analyst will not rely exclusively on the chromatogram or quantitation report.
   j) Typically the lower value from the two analytical columns will be reported due to the possibility of coelution inflating the higher result. However, during data reduction the analyst should evaluate both columns and choose the appropriate value. For example, hydrocarbons can cause troughs in the chromatogram. If a peak area is affected by a nearby trough, the area will be biased low and will not represent concentration present.
   k) In many cases, non-target matrix interference will obscure all or part of the target chromatographic region. When this occurs, the analyst may reanalyze the extract more dilute or may choose to raise report limits to reflect what levels could be determined above the interference. Adjusting report limits for interference requires experience and knowledge of the herbicides analytical system.
   l) During data reduction analyst should check that all hits are within calibration range.
   m) The analyst should develop a consistent/logical procedure for reducing data which can be reviewed and understood by other GC analysts and data reviewers. Generally, data reduction is documented on the "working" quantitation reports which are kept in the data folder. Any special notes, comments or additional data may also be documented and filed in the data folder for archival
   n) An example of quantitation report is shown in appendix F.

9. Data Reporting
   a) Recoveries will be reported to 2-3 significant digits.
   b) Results will be reported to 1-2 significant digits.
   c) Soil results will be reported as dry weight (corrected for percent moisture).
   d) All results will be corrected for dilutions.
   e) All results will be corrected for amount extracted if less than normal.
   f) Deliverables will vary with QC level.

CALCULATIONS

Equation 1. Percent Difference Calculation

$$\textit{Percent Difference} = \frac{RRF_{average} - RRF_{cont\ cal}}{}$$

RRFaverage

Where: RRFaverage is the average relative response factor, and RRFcont cal is the relative response factor of the continuing calibration

Equation 2. Curve Calculations

For a Linear Curve = $y = ax + b$

For a Quadratic Curve: $y = ax^2 + bx + c$

Where a is the slope, x is the x intercept, b is the y intercept, and c is a constant

Equation 3. Dry Weight Correction

$$D(dry\ weight) = \left(\frac{100 - \%Moisture}{100}\right)$$

Equation 4. Corrected quantitation

$$Corrected\ Quantitation\ (dry\ result) = \frac{\mu g\ /\ Kg\ (wet\ result)}{D(dry\ weight)}$$

Equation 5. Percent Resolution

$$\%\ Resolution = \left(\frac{Ht_{\ valley}}{Ht_{\ smaller\ peak}}\right) x\ 100$$

Equation 6, Calculation for soils

$$Concentration\ in\ ug/Kg = \frac{(R(x)(Vf)(10\text{-}3\ ug/ng)(DF)}{(WT)}$$

Where DF is the diliution factor, WT is the weight in grams, Vf is the final volume, and R(x) is the instrument result.

Equation 7, Calculation for waters

Concentration in ul/L=R(x)(DF)(Vf/(Vo)

Where DF is the dilution factor, Vf is the final volume, and Vo is the intial volume, R(x) is the instrument result.

REVIEW

The analyst is most familiar with the data and analyst review occurs throughout the analytical process.

After analysis, data is reviewed by another analyst. The reviewing analyst must be familiar with the method, SOP requirements, and pesticide data interpretation. Calibration and QC data should be evaluated for acceptability. Sample chromatographic data should be evaluated for acceptability.

The sample data must be reviewed with the associated quality control data. The following items should be checked before reporting sample results.

1. Valid initial calibration
2. Valid continuing calibration
3. Acceptable method blank
4. Acceptable MS/MSD and Blank Spike (LCS)
5. Acceptable surrogate recoveries according to control chart limits
6. Results corrected for dilutions
7. Results for soil/sediments corrected for dry weight (unless client specifies reports be based on wet weight)
8. Chromatographic data integration and interpretation (evaluate possible carryover, peak shape, retention time, surrounding chemical noise)
9. All appropriate exception reports are completed and routed

The final package and case narrative is reviewed for completeness and acceptability.

CORRECTIVE ACTION

Unacceptable initial calibration requires appropriate corrective action and reanalysis of the initial calibration. Corrective action will be vary and be dependent on problem determined to have caused unacceptable initial calibration.

Unacceptable continuing calibration verification requires appropriate corrective action and reanalysis of affected samples. Corrective action will be vary and be dependent on problem determined to have caused unacceptable continuing calibration.

Unacceptable surrogate recovery requires investigation. Surrogate recovery is calculated for all samples, blanks, and spikes. Some samples will be diluted for analysis, diluting out the surrogates and therefore recovery cannot be determined. Calculated recoveries should be within laboratory generated recovery limits.

1. One surrogate compound is spiked. 2,4-dichlorophenyl acetic acid is evaluated as the primary surrogate.
2. If recoveries are not within acceptance limits, calculations should be verified. The surrogate spiking solution concentration, amount added, and actual concentration calculation should be evaluated for errors.
3. High recoveries may be attributed to interfering peaks. Chromatograms will be examined for chromatographic interference. Recovery from both analytical columns may be evaluated.
4. Familiar samples with a history of non-compliant surrogate recovery may not require further corrective action.
5. Analyst should determine if the problematic sample has a field duplicate or matrix spike/matrix spike duplicate. If non-compliant recovery is reproduced in a field duplicate or MS/MSD, the sample has already been extracted more than once and matrix effect may be assumed.
6. Extraction logs should be examined for difficulties noted during sample preparation (i.e., emulsions).
7. Extract may be reanalyzed to verify result.

8. If investigation does not provide explanation, sample should be re-extracted if adequate sample volume is available.

Unacceptable spike recovery requires investigation. Matrix spike and matrix spike duplicates are subject to matrix effects and therefore established limits are advisory. Unless analyst error is obvious and MS/MSD results are reproducible, no corrective action is required. Blank spikes (LCS) have no matrix effect and will require corrective action for unacceptable results.

The case narrative should explain any variations from standard analysis.

DOCUMENTATION

Preparation of the sample extract is documented in a bound extraction logbook. A copy of the extraction log is included with the batch file.

Each GC has its own bound maintenance journal. This journal contains records of instrument maintenance, repair, and modifications. Each entry will be dated and signed by the analyst.

Each GC has its own bound sample injection log book. All initial calibration, continuing calibration, and sample injections are entered. Each entry contains the run number (unique file name), date of analysis, analyst, microliters injected, sample identification, acquisition method file (chromatographic method) reference, and chromatographic conditions. The raw data files and acquisition method files are archived onto magnetic tape and then deleted from the hard disk after review is complete. Appendix D is an example injection logbook page.

HEALTH AND SAFETY

Any unfamiliar water sample may offer dangerous contents beyond the list of chemicals listed in this SOP. All samples and extracts should be treated as potential health hazards and handled with proper precautions.

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

PEL maintains a reference file of material data handling sheets that is made available to all personnel involved in the chemical analysis. Refer to the "general safety " SOP for additional reading on laboratory safety .

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

14. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Update II, Method 8151.
15. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Update III, Method 8151A.
16. HQ Air Force Center for Environmental Excellence (AFCEE) Quality Assur. Proj. Plan (QAPP), Version 3.0

Appendix A
Typical Initial Calibration Sequence of Injections (injections may be in different order)

1. Instrument Blank
2. Single-component mix - Level 1 (all single peak targets and surrogates)
3. Single-component mix - Level 2 (all single peak targets and surrogates)
4. Single-component mix - Level 3 (all single peak targets and surrogates)
5. Single-component mix - Level 4 (all single peak targets and surrogates)
6. Single-component mix - Level 5 (all single peak targets and surrogates)
7. Single-component Historical - 2nd Source Check

Appendix B
Typical Analytical Sequence of Injections (following successful initial calibration)

1. Instrument Blank
2. Calibration Blank
3. Mid-level of single-component herbicide mix
4. Method Blank
5. Reagent MS
6. Reagent MSD
7. LCS
8. Extract 1
9. Extract 1MS
10. Extract 1MSD
11. Extract 2
12. Extract 3
13. Extract 4
14. Extract 5
15. Extract 6
16. Extract 7
17. Extract 8
18. Extract 9
19. Extract 10
20. Single-component mix – mid-level
21. Extract 11
22. Extract 12
23. Extract 13
24. Single-component mix – mid-level (required for AFCEE work)

Appendix C
Instrument Configuration and Conditions

XTI-5 (0.53mm ID, 0.50µm film thickness), approximately 30 meters
RTX-1701 (0.53mm ID, 0.50µm film thickness), approximately 30 meters

Appendix D
Example of Instrument Injection Logbook

Internal		Method Files(s)				Sequence	
A		E		H		X	
B		F		I:		Y	
C		G		J:		Z	

Inj	C	Anal	Initia	μL	Anal	Lab	Treatm	IS	ME	SE	Comme	GC Config. &
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Appendix E
Variations to this SOP for AFCEE 3.0 Analysis

Since the AFCEE QAPP 3.0 is very specific, all information available in the QAPP will not be repeated in this SOP. Anyone dealing with AFCEE should have a copy of the QAPP and be familiar with its contents. Variations that will be taken from this SOP in analyzing samples for AFCEE 2.0 are summarized below.

1. Extraction
   a) Holding times will be met according to the time of sample collection (with correction for time zone differences).
   b) Sample extraction time will be recorded in addition to extraction date.

2. Calibration
   a) Initial calibration correlation coefficient criteria listed in this SOP is not valid. Three options provided for in AFCEE QAPP
      i) Curve must have mean ≤ 20% RSD for all analytes. With no single analyte 30%.
      ii) Linear – least squared regression, r > 0.995
      iii) Non-Linear – coefficient of determination ≥ 0.990
         (1) 6 points used for second order equation.
         (2) 7 points must be used for a third order equation.
   b) Second vendor standards must be ≤ 15% difference.
   c) Low point of initial calibration must be at or below AFCEE report limits.

3. Surrogates
   a) Acceptability is not based on laboratory established limits.
   b) Acceptance limits for waters and soils are listed in AFCEE QAPP.

4. Spikes
   a) MDL must be less than one-half of AFCEE report limit.
   b) Multiple spikes (LCS, MS, MSD) will be prepared depending on requested target list.
   c) Matrix spike and matrix spike duplicates (MS/MSD) will be prepared as requested by project.
   d) Single-component pesticide spikes (LCS, MS, MSD) will be extracted and analyzed when pesticides are targets.
   e) Toxaphene spikes (LCS, MS, MSD) will be extracted and analyzed when toxaphene is a target.
   f) Acceptability is not based on laboratory established limits
   g) Acceptance limits for waters and soils are listed in AFCEE QAPP.

5. Confirmation
   a) Although data is qualified to MDL, only hits above the AFCEE report limit must be confirmed.

6. Data Reduction/Reporting
   a) AFCEE report limits are listed in the AFCEE QAPP and are different from standard lab limits.
   b) Data are qualified to the MDL based on instructions in AFCEE QAPP.
   c) Although data are qualified to MDL, only hits above the report limit must be confirmed.
   d) Significant figure rules do not apply. AFCEE requires that MDLs and results be reported to one more decimal place than AFCEE report limit without regard to significant digits.
   e) MDLs and report limits are not corrected for dry weight or dilution on the Form O-2.
   f) Qualifiers are applied to results based on instructions in AFCEE QAPP.
   g) AFCEE deliverables are designated in AFCEE QAPP.
   h) AFCEE deliverables are not summarized in Appendix E of this SOP.

7. Corrective action is identified in the AFCEE QAPP

PEL Laboratories, Inc. - Standard Operating Procedure

Sample Analysis: chloride
Method 325.2 (colorimetric, automated ferricyanide)

APPROVED:

Sample Prep. Section Leader — Date

QA Officer — Date

Laboratory Director — Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. for the determination of chloride in drinking, surface, and saline waters, domestic and industrial wastes, and soils.

The practical range of determination is 1 to 100 mg Cl/L, this range may be extended by diluting the sample.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

Method Summary

Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in concentration proportional to the original chloride concentration. This ion absorbs strongly at 480 nm.

Since the presence of chlorides is determined by color formation, any presence of color in the samples will create interference. Colored samples should be appropriately diluted to reduce this interference.

QA/QC REQUIREMENTS

The holding time for this test is 28 days.

This SOP was written to conform to all QA/QC criteria described in the following methods: EPA 325.2

The following control samples should be run with each batch of samples.

1. Method Blank: used to check for any contamination within the analytical system.
2. Initial Calibration Verification (ICV): True value is given and percent recovery is calculated. The recovery on the ICV must be within 10% of the true value for acceptance. Each batch must begin with an ICV and be followed by a Continuing Calibration Verification (CCV) sample at the end of the batch. In addition, a CCV is run every ten samples to verify the calibration curve.
3. Initial Calibration Blank (ICB): A sample blank is run immediately following the ICV to check for contamination within the system. In addition, a Continuing Calibration Verification (CCB) is run at the end of the batch as well as every ten samples to check for contamination within the system and carryover from sample to sample.
4. Laboratory Control Sample (LCS): The ICV/ICB is followed by a Laboratory Control Sample, which is derived from a different source as the calibration curve. The true value is given and the percent recovery is calculated. The recovery on the LCS sample must be within 80 – 120%. When the recovery is outside of this range, the system must be checked, a new LCS sample made up, and the associated blank and batch of samples are re-

analyzed. Any out of control event that references client data must be documented in the case narrative (Level II, III, and IV packages) and/or a corrective action report (CAR) form.

5. Matrix Spikes (MS) and Matrix Spike Duplicates (MSD): Matrix Spikes and Matrix Spike Duplicates are run every twenty samples. The MS and MSD must have a percent recovery between 75 – 125%. In addition, the RPD between the MS and MSD must be less then 20%.

EQUIPMENT/APPARATUS

1. Lachat QuikChem 8000 Automated Flow Injection Analyzer which includes:
   a. Automatic sampler
   b. Proportioning pump
   c. Injection module with an 18.5 cm 0.8 mm i.d. sample loop.
   d. Colorimeter detector:
      i. Flow Cell, 10 mm, 80 µL
      ii. Interference Filter Wavelength, 480 nm
   e. Reaction module or manifold 10-117-07-1-B
   f. Data System

REAGENTS

1. Chloride Color Reagent: Mercuric Thiocyanate 0.06% Solution
2. Deionized Water: Used as the carrier as well as for the ICB / CCB and the method blank.
3. Standard chloride solution 1.00 mL = 1.00 mg CL (1000 ppm).

PROCEDURE

No advance sample preparation is required. Set up manifold as shown in **Error! Reference source not found.**.

FIGURE 1

CARRIER is deionized water.
2.5" is **168** cm of tubing on a 2.5-in coil support
All manifold tubing is 0.8 mm (0.032 in) i.d. This is 5.2 uL/cm

1. Open Omion program, if closed. Type in user name and password
2. Open Analyte Table for Chloride.
3. Under Method, Set Injection Timing:
   a. Pump speed: 35
   b. Cycle period: 55.0 s
   c. Load period: 9.0s
   d. Inject period: 46.0 s
   e. Inject to start of peak period: 5.0 s
   f. Inject to end of peak period: 25.0 s
4. Preparation of Calibration Curve:
   a. Prepare calibration curve using 500 mg/L standard chloride solution.

b. Dilute standards as follows:

mL standard / 100 mL Deionized	Final concentration of standard
0 mL	0 mg/L
0.1 mL	0.5 mg/L
1.0 mL	5 mg/L
4.0 mL	20 mg/L
8.0 mL	40 mg/L
16.0 mL	80 mg/L

c. The calibration curve fit type, is 2nd order Poly

d. The correlation coefficient must be ≥ 0.995

5. System Operation:

a. Inspect manifold and tubing for proper connections.

b. Turn on power.

c. Place manifold tubing into pump tube cassettes.

d. Place reagent feedlines into proper containers. Raise tension levers on pump tube cassettes.

e. Pump reagents through system until a stable baseline is attained.

f. Set up sample tray, by placing calibration standards and the blank in descending order of concentration, followed by unknowns and necessary QC.

g. Save tray as – Cl and the date of the run, ex. Cl063000.

h. Open calibration curve, go to fit and hit clear.

i. Run tray.

j. At end of run, place all feedlines in water for 5–10 minutes, flush system, remove and pump dry.

k. Turn off pump, all manifolds, and release tension levers on pump tube cassettes.

CALCULATION

Standard curve is prepared by plotting peak heights of processed standards against known concentrations. Concentration of samples is computed by comparing sample peak heights or peak area with standard curve.

REVIEW/VALIDATION

Data review and validation must be reviewed by the section supervisor according to PEL Laboratories, Inc. Quality Manual. After the data review process has been completed, copies of the data logbook are made from the LIMS environment.

REPORTING

Chloride results are reported in units of mg/L.

Values below 1 mg/L are reported as non-detect, (ND).

All analysis data should be recorded in the Lachat logbook. All pertinent information such as sample size, dilution factors, date(s) of analysis, and sample ID is included. As the analysis proceeds, problems, variations, and other information are written in the logbook immediately.

DOCUMENTATION

Documentation must follow the requirements in PEL Laboratories' Quality Manual SOP00040-QA; *Rules for Documentation.*

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

- Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, March 1983. Method 325.2

PEL Laboratories, Inc. - Standard Operating Procedure

Sample Analysis: Nitrogen, Nitrate
Method 353.2 (Colorimetric, Automated, Cadmium Reduction)

APPROVED:

Sample Prep. Section Leader — Date

QA Officer — Date

Laboratory Director — Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. for the determination of nitrate and nitrite combined in surface and saline waters, and domestic and industrial wastes.

The applicable range of this method is 0.02-to 2.0 mg/l nitrate nitrogen. The range may be extended with sample dilution.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

Interferences

Residual chlorine can oxidize the cadmium column.

Low results might be obtained from samples that contain high concentrations of iron, copper, or other metals. EDTA is added to the samples to eliminate this interference.

Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

Method Summary

Nitrate is reduced to nitrite by passing through a copperized cadmium column. The nitrite is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. This creates a magenta color, which is read at 520 nm. The nitrite is then subtracted from the total nitrate-nitrite total, to determine the amount of nitrate. If nitrate-nitrite requested, do not subtract the nitrite and report the result as nitrate-nitrite

QA/QC REQUIREMENTS

If the individual nitrite or nitrate analyses are performed, the sample is not preserved, other than refrigeration at 4°C, and the holding time is 48 hours from the time of sampling. The holding time for nitrate can be extended to 28 days by preserving the sample with 2 mL H2SO4 after nitrite analysis is preformed.

This SOP was written to conform to all QA/QC criteria described in the following methods: EPA 353.2.

The following control samples should be run with each batch of samples. A batch is defined as 20 field samples, or 18 field samples for AFCEE:

1. Method Blank: An analyte free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. Used to check for any contamination within the analytical system.
2. Initial Calibration Verification (ICV): A standard is used to verify the calibration curve. True value is given and percent recovery is calculated. The recovery on the ICV must be within 10% of the true value for acceptance. Each analysis batch must begin with an ICV and be followed by a Continuing Calibration Verification (CCV) sample at the end of the batch. In addition, a CCV is run every ten samples to verify the stability of the system.
3. Initial Calibration Blank (ICB): An analyte free matrix that is the same as the carrier for the test. A sample blank is run immediately following the ICV to check for contamination within the system. In addition, a Continuing Calibration Verification (CCB) is run at the end of the batch as well as every ten samples to check for contamination within the system and carryover from sample to sample.
4. Laboratory Control Sample (LCS): A second source standard of known matrix, spiked with analytes and carried through the preparation and analysis procedure as a sample. A Laboratory Control Sample follows the ICV/ICB, the true value is given and the percent recovery is calculated. The recovery of the LCS sample must be within 80 – 120%. When the recovery is outside of this range, the system must be checked, a new LCS sample made up, and the associated blank and batch of samples are reanalyzed. Any out of control event that references client data must be documented in the case narrative (Level II, III, and IV packages) and/or a corrective action report (CAR) form. Two LCS samples are analyzed in this method, one spiked with NO_2 and one spiked with NO_3. The efficiency of the cadmium column is determined by dividing the NO_2 LCS recovery by the recovery from the NO_3 LCS and multiplying by 100%.
5. Matrix Spikes (MS) and Matrix Spike Duplicates (MSD): Matrix Spikes and Matrix Spike Duplicates are aliquots of sample spiked with a known concentration of target analytes. MS and MSD are run every batch. The MS and MSD must have a percent recovery between 75 – 125%, of the sample plus the known spike concentration. In addition, the RPD between the MS and MSD must be less then 20%.

EQUIPMENT/APPARATUS

1. Lachat QuikChem Automated Flow Injection Ion Analyzer which includes:
   a. Automatic Sampler
   b. Proportioning Pump
   c. Nitrate-Nitrite Injection Module with a 17 cm, 0.80 mm i.d. sample loop.
   d. Nitrite Injection Module with a 10 cm, 0.80 mm i.d. sample loop.
   e. Colorimeter detector:
      i. Interference Filter Wavelength: 520 nm (2)
      ii. Flow Cell: 10 mm, 80 uL (2)
   f. Reaction Module or manifold 10-107-04-1-C with Cd column
   g. Reaction Module or manifold 10-107-05-1-A
   h. Data System
2. 1 Liter volumetric flasks
3. 250 mL volumetric flasks
4. 100 mL volumetric flasks
5. 45 micron filters, to filter samples prior to analysis

REAGENTS

1. Deionized Water (ASTM Type II)

2. 15 N Sodium Hydroxide: Add 150 g of NaOH to 250 Liter volumetric flask, dilute with deionized water. **CAUTION** this solution will get very HOT! Store in a plastic bottle for up to two months.
3. Ammonium Chloride Buffer, pH 8.5: Dissolve 85.0 g ammonium chloride and 1.0 g disodium ethylenediamine tetraacetic dihydrate in a 1 Liter volumetric flask. Dilute to the mark with deionized water. Adjust the pH to 8.5 by using 15 N NaOH solution (reagent #2).
4. Sulfanilamide color reagent: Add 100 mL 85% phosphoric acid, and dissolve 40.0 g sulfanilamide and 1.0 g N-(1-naphthyl)ethylenediamine dihydrochloride, in a 1 Liter volumetric flask. Dilute to the mark with deionized water. Store in a dark bottle, this solution is stable for 1 month.
5. Stock Nitrate standard 1000 mg N/L as NO_3. One stock standard is used for the Calibration curve, as well as the ICV, CCV and MS/MSD. A second source stock nitrate standard is used for the LCS. Dilute as shown in **Table 1**.
6. Stock Nitrite standards 250 mg N/L as NO_2. One stock standard is used for Column efficiency LCS. Dilute as shown in **Table 1**

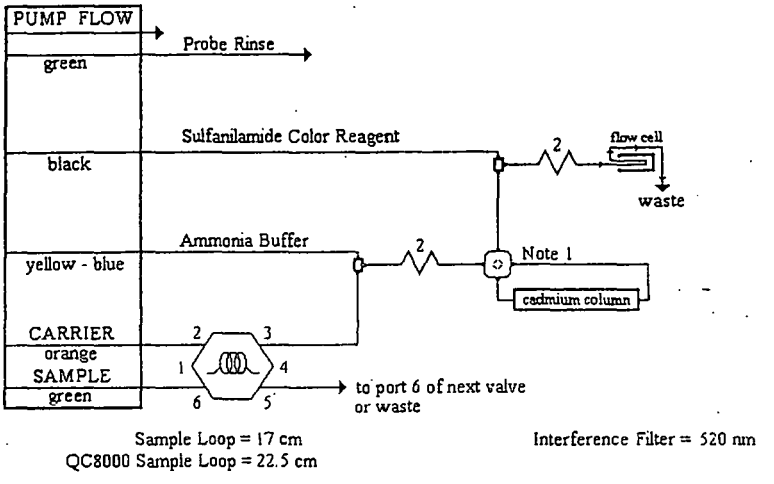
PROCEDURES

No advanced sample is required.

1. Set up manifolds as shown in **FIGURE 1**

FIGURE 1

Nitrate-Nitrite Channel



CARRIER is deionized water

2 is **70** cm tubing on a 4.5 cm coil support

2" is **135** cm tubing on a 2 in coil support

All manifold tubing is 0.8 mm (0.032 in) i.d. This is 5.2 uL/cm

2. Open Omnion program, if closed. Type in user name and password.
3. Open Analyte Table for Nitrate.
4. Under Method, Set Injection Timing for each channel:
   a. Pump speed: 35
   b. Cycle period: 50.0 s
   c. Load period: 10.0s
   d. Inject period: 40.0 s
   e. Inject to start of peak period: 18.0 s
5. Preparation of nitrite LCS. Reagent (#6) pipette out o.4mL/100 ml voL flask diluted to 100 ml with DI water. LCS = 1 ppm nitrite.
6. Preparation of nitrate LCS. From Reagent (#5 second source) make 10 ppm an intermediate by pipetting out 1mL/100 ml volt. Flask diluted to 100 ml DI water. From the intermediate pipette out 10mL/100 mLvoL. Flask diluted to 100 mL DI water. LCS =1 ppm. ICV, and CCV done the same way from reagent (#5)
7. Preparation of Calibration curve:
   a. Prepare calibration curve using the Nitrate intermediate in step 6. Standard (reagents #5)

NO_3 Standard

ML standard / 100 mL Deionized H_2O	Final concentration of standard
0 mL	0 mg/L
0.2 mL	0.02 mg/L
2.5 mL	0.250 mg/L
5.0 mL	0.500 mg/L
10.0 mL	1.00 mg/L
20.0 mL	2.00 mg/L

   b. The calibration curve fit type is 1st order Polynomial.
   c. Both correlation coefficients must be greater then or equal to 0.995.
8. System Operation:
   a. Inspect manifold and tubing for proper connections.
   b. Turn on power.
   c. Place manifold tubing into pump tube cassettes.
   d. Make sure the switch for the cadmium column is in the OFFLINE position
   e. Place reagent feed lines into proper containers. Raise tension levers on pump tube cassettes.
   f. Pump reagents through system until a stable baseline is attained.
   g. Once, the buffer solution has gone completely through the manifold, turn the switch for the cadmium column to the ONLINE position.
   h. Set up sample tray, by placing calibration standards and the blank in descending order of concentration, followed by unknowns and necessary QC. A sample tray is shown in **FIGURE 2.**
   i. Save tray as – NN and the date of the run, ex. NN063000.

j. Open calibration curve, go to fit and hit clear.

k. Run tray.

l. At end of run, turn switch for cadmium column to OFFLINE position and place all feed lines in water for 5–10 minutes, flush system, remove and pump dry.

m. Turn off pump, all manifolds, and release tension levers on pump tube cassettes.

9. SYSTEM NOTES

a. The Cd column efficiency should be between 80 percent and better if working properly. This is checked by analyzing a nitrate LCS and a nitrite LCS, and calculating as shown below.

$$(NO_3\ LCS\ /\ NO_2\ LCS) * 100\% = \text{efficiency of cadmium column}$$

FIGURE 2

Sample Number	Sample	Comments
	ICV	90 to 110% Recovery
	ICB	|ICB| < MDL
1	PBA	|PBA| < MDL
2	LCS – NO_2	80 to 120% Recovery
3	LCS – NO_3	80 to 120% Recovery
4	Sample 1	
5	Sample 2	
6	Sample 3	
7	Sample 4	
8	Sample 5	
9	Sample 5 MS	75 to 125% Recovery
10	Sample 5 MSD	RPD of < 20%
	CCV	90 to 110% Recovery
	CCB	|CCB| < MDL
11	Sample 6	
12	Sample 7	
13	Sample 8	
14	Sample 9	
15	Sample 10	
16	Sample 11	
17	Sample 12	
18	Sample 13	
19	Sample 14	
20	Sample 15	
	CCV	90 to 110% Recovery
	CCB	|CCB| < MDL

CALCULATIONS

Standard curve is prepared by plotting peak area of processed standards against known concentrations. Concentration of samples is computed by comparing sample peak heights or peak area with standard curve.

Enter the data from Data System into the spreadsheet in Excel to calculate the amount of nitrate in the samples.

REVIEW/ VALIDATION

Data review and validation must be reviewed by the section supervisor according to PEL Laboratories, Inc.'s Quality Manual. After the data review process has been completed, copies of the data logbook are made from the LIMS environment.

REPORTING

Nitrate/Nitrite results are reported in units of mg/L.

All analysis data should be recorded in the Lachat logbook. All pertinent information such as sample size, dilution factors, date(s) of analysis, and sample ID is included. As the analysis proceeds, problems, variations, and other information are written in the logbook immediately.

DOCUMENTATION

Documentation must follow the requirements in PEL Laboratories' Quality Manual and SOP00040-QA; *Rules for Documentation.*

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

- Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, March 1983. Method 353.2
- SOP G-00040-QA, *Rules for documentation*

PEL Laboratories, Inc - Standard Operating Procedure

Sample Analysis: Sulfate, Method EPA 375.4 (Turbidimetric)

APPROVED:

Sample Prep. Section Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc to determine sulfate in drinking and surface waters, domestic and industrial wastes. The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4/L.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

Method Summary

The sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a spectrophotometer or filter photometer and compared to a curve prepared from standard sulfate solutions.

Silica in concentrations over 500 mg/L will interfere.

Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted

QA/QC REQUIREMENTS

The holding time for this test is 28 days.

Preserve by refrigeration at 4°C.

This SOP was written to conform to all QA/QC criteria described in the following method: EPA 375.4

Table 1, contains an analytical batch including the necessary QC

For sulfate analyses, the following control samples are run with each batch of samples. A batch is defined as 20 field samples or 18 field samples for AFCEE:

1. Method blank - used to check for contamination within the prep and analytical system.
2. Initial Calibration Verification (ICV) - True value is given and the % recovery is calculated. The recovery on the ICV sample must be within 10% of the true value for acceptance. Each batch must begin with an ICV, and must be followed by a Continuing Calibration Verification (CCV) sample at the end of the batch. In addition to this a CCV is run every three to four samples in order to verify the calibration curve.
3. Initial Calibration Blank (ICB): A sample blank is run immediately following the ICV to check for contamination within the system. In addition, a Continuing Calibration Blank (CCB) is run at the end of the batch as well as every ten samples to check for contamination within the system and carryover from sample to sample.

4. Laboratory Control Sample (LCS) - The ICV / ICB is followed by a Laboratory Control Sample, which is derived from a different source as the calibration curve. The true value is given and the % recovery is calculated. The recovery on the LCS sample must be within 20% of the true value for acceptance. When the recovery is outside this range, the system must be checked, a new LCS sample made up, and the associated batch of samples must be re-analyzed. An LCS must be analyzed each batch.

5. Matrix Spikes (MS) and Matrix Spikes Duplicates (MSD) - Matrix Spikes and Matrix Spike Duplicates are run with every batch. The MS and MSD must have a Percent Recovery of 75 to 125 %. An RPD greater then 20%, between the MS and MSD is considered the outside limit. If the RPD is outside of this likmit the batch and its associated samples must be reanalyzed.

Table 1

Sample #	Sample	Comments
	ICV	90 to 110 % Recovery
	ICB	|ICB| < MDL
1	PBA	|PBA| < MDL
2	LCS	80 to 120% Recovery
3	Sample 1	
4	Sample 2	
	CCV	90 to 110 % Recovery
5	Sample 3	
6	Sample 4	
7	Sample 4 MS	75 to 125 % Recovery
8	Sample 4 MSD	RPD of <20 %
9	Sample 5	
10	Sample 6	
	CCV	90 to 110 % Recovery
	CCB	|CCB| < MDL
11	Sample 7	
12	Sample 8	
13	Sample 9	
14	Sample 10	
	CCV	90 to 110 % Recovery
15	Sample 11	
16	Sample 12	
17	Sample 13	
18	Sample 14	
	CCV	90 to 110 % Recovery
19	Sample 15	
20	Sample 16	
	CCV	90 to 110 % Recovery
	CCB	|CCB| < MDL
21	PBA	|PBA| < MDL
22	LCS	80 to 120 % Recovery
23	Sample 17	
24	Sample 18	
	CCV	90 to 110 % Recovery

EQUIPMENT/APPARATUS

1. Magnetic stirrer, variable speed so it can be held constant just below splashing. Use identical size and shape stirring bars.
2. Stopwatch or accurate timer.
3. Measuring spoon, capacity 0.2 to 0.3 mL.
4. Hach Model 3000 Spectrophotometer set at 450 nm and a light path of exactly 2.54 cm (1 inch).

REAGENTS

1. Conditioning reagent: Place 30 mL concentrated HCl, 300 mL distilled water, 100 mL 95% ethanol or isopropanol and 75 g NaCl in solution in a container. Add 50 mL glycerol and mix.
2. Barium chloride, $BaCl_2$, crystals, 20 to 30 mesh. (ACS grade)
3. Standard sulfate solution 1.00 mL = 1.00 mg SO_4 (1000 ppm SO_4).

PROCEDURE

1. Preparation of calibration curve:
   a. Prepare calibration curve using standard sulfate solution.
   b. Dilute standards as follows:

ML stock / 25 mL	Final concentration of standard
0 mL	0 mg/L
0.125 mL	5 mg/L
0.250 mL	10 mg/L
0.500 mL	20 mg/L
1.000 mL	40 mg/L

2. Formation of barium sulfate turbidity at 450 nm.
   a. Read all samples in the spectrometer, prior to addition of barium chloride, in order to correct for sample turbidity.
   b. Place 25.0 mL sample or a suitable portion diluted to 25.0 mL into a suitable container for mixing.
   c. Add exactly 1.0 mL conditioning reagent.
   d. Place stirring bar in solution and mix on the magnetic stirring apparatus.
   e. While the mixture is being stirred, add a measuring spoonful of $BaCl_2$ crystals and begin timing immediately.
   f. Stir exactly 1.0 minute at constant speed, on the magnetic stirring apparatus.
3. Measurement of barium sulfate turbidity at 450 nm.
   a. Immediately after the stirring period has ended, pour the solution into a Hach sample cell (path length = 2.54 cm).
   b. Measure turbidity at 30-second intervals for 4 minutes.
   c. Record both the maximum absorbance and the corresponding concentration reading obtained in the 4-minute period within the Sulfate Logbook.

CALCULATIONS

Read mg SO_4/L from calibration curve, using the PE spreadsheet program.

REVIEW/VALIDATION

Data review and validation must be reviewed by the section supervisor according to PEL Laboratories, Inc Quality Manual. After the data review process has been completed, copies of the data logbook are made for data entry personnel. The logbook is returned to the analyst and report forms are generated from the LIMS environment.

REPORTING

a. Sulfate is reported in units of mg/L and must be reported with the corresponding dilution factor.

b. Samples with values lower than the Method Detection Limit (MDL) or Reporting Limit (RL) are reported as Non-Detected (ND).

c. Samples with values higher than 40 mg/L (or the highest calibration point) must be diluted and re-analyzed.

DOCUMENTATION

Documentation must follow the requirements in PEL Laboratories' Quality Manual and SOP00040-QA; *Rules for Documentation.*

Record all data in analyst's notebook before beginning any analyses. Include all pertinent information such as sample size, dilution factors, dates of analysis, and sample ID. As the analysis proceeds, problems, variations, and other information are written in the logbook immediately.

Copies of all reviewed data are given to the data reporting personnel for generation of data deliverables.

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staffs are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

- *Methods for Chemical Analysis Water and Wastes*, U.S. EPA, 600/4-79-020, March 1983, Method 375.4

PEL Laboratories, Inc. - Standard Operating Procedure

Sample Analysis: Titration Procedure for Sulfides,

APPROVED:

Sample Prep. Section Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. to determine total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes. Acid insoluble sulfides in water are not measured by the use of this test. (Copper sulfide is the only common sulfide in this class). This method is suitable for the measurement of sulfide in concentrations above 1 mg/L in a water sample.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

Summary Of Method

1. For water samples excess iodine is added to a sample which may or may not have been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions.
2. The excess iodine is back titrated with sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is not possible because of oxidative degradation, quantitation is based on the sodium thiosulfate.

Interferences

Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances will give high results. Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an immeasurable form. If the sample is not preserved with zinc acetate and NaOH, the analysis must be started immediately. Similarly, the measurement of dissolved sulfides must also be commenced immediately.

QA/QC REQUIREMENTS

The holding time for this test is 7 days, from the time of sampling.

This SOP was written to conform with all QA/QC criteria described in the following method: 376.1

EQUIPMENT/APPARATUS

1. 500 mL flasks.
2. Magnetic stirrer.
3. Burettes, 25 or 50 mL volume.
4. Volumetric pipettes.
5. Class A 100 mL graduated cylinders.

REAGENTS

1. ASTM Type II Reagent Water

2. Starch solution – purchased commercially.
3. Iodine solution (approximately 0.025N)
4. Dissolve 25 g potassium iodide, KI, in 700 mL of reagent water in a 1-liter volumetric flask. Add 3.2 g iodine, I2. Allow to dissolve. Add the type and amount of acid specified in Step 7.3.2. Dilute to 1 liter and standardize as follows.
5. Dissolve approximately 2g KI in 150 mL of reagent water. Add exactly 20 mL of the iodine solution (Step 5.10.1) to be titrated and dilute to 300 mL with reagent water.
6. Titrate with 0.025N standardized sodium thiosulfate until the amber color fades to yellow. Add starch indicator solution. Continue titration drop by drop until the blue color disappears. Sodium Thiosulfate is purchased commercially.
   a. Run in replicate.
7. Calculate the normality as follows using Equation 1
8. Sodium sulfide nonanhydrate, $Na_2S \bullet 9H_2O$. For the preparation of standard solutions to be used for calibration curves. Standards must be prepared at pH > 9 and < 11. Protect standard from exposure to oxygen by preparing it without headspace. These standards are unstable and should be prepared daily.
9. Titrant
   a. Standard sodium thiosulfate solution (0.025N), $Na_2S_20 \bullet 5H_20$. Dissolve 6.205 + 0.005 g $Na_2S_20_3 \bullet 5H_20$ in 500 mL reagent water. Add 9 mL lN NaOH and dilute to 1 liter. This solution is also commercially available.

PROCEDURE

1. Standards
   a. Place a known amount of standard iodine solution into a 125 mL flask. The amount should be estimated to be in excess of the amount of sulfide expected.
   b. Add 20 mL of deionized water to the flask.
   c. Add 2 mL of 6N HCl.
   d. Inject the standard under the surface of the solution.
   e. Add 100 mL of deionized water to the flask, pouring the water so that it runs down the side of the flask.
   f. If the iodine color disappears, add more iodine until the color remains. Record the total number of milliliters of standard iodine used.
   g. Add 5 drops of starch indicator to obtain a blue color.
   h. Titrate with the reducing solution (0.0250 N sodium thiosulfate). Record the number of milliliters used.
   i. Calculate the concentration of sulfide in the sample using Equation 2.
   j. Calculate the calibration coefficient using the sulfide spreadsheet in Excel. The coefficient must be greater than or equal to 0.995.
2. Samples
   a. Place a known amount of standard iodine solution into a 125 mL flask. The amount should be estimated to be in excess of the amount of sulfide expected.
   b. Add 20 mL of deionized water to the flask.
   c. Add 2 mL of 6N HCl
   d. Add 100 mL of sample to the flask, pouring the sample so that it runs down the side of the flask.
   e. If the iodine color disappears, add more iodine until the color remains. Record the total number of milliliters of standard iodine used.

f. Add 5 drops of starch indicator to obtain a blue color.

g. Titrate with the reducing solution (0.0250 N sodium thiosulfate). Record the number of milliliters used.

h. Calculate the concentration of sulfide in the sample using Equation 2

CALCULATIONS

One mL of 0.0250 N standard iodine solution reacts with 0.4 mg of sulfide present in the titration vessel.

Equation 1. Calculation of Normality of KI Titration Solution.

$$Nomality\ (I_2) = \frac{mL\ of\ titrant\ x\ normality\ of\ titrant}{sample\ size\ in\ mL}$$

Equation 2. Calculation of Sulfide Concentration in Sample.

$$\frac{(mL\ I_2\ x\ N\ I_2) - (mL\ titrant\ x\ N\ titrant)\ x\left(\frac{32.06\ g}{2\ eq.}\right)}{sample\ weight\ (kg)\ or\ sample\ volume\ (L)} = sulfide\ (mg/kg)\ or\ (mg/L)$$

REVIEW/VALIDATION

Data review and validation must be reviewed by the section supervisor, according to PEL Laboratories, Inc. Quality Manual. After the data review process has been completed, copies of the data logbook are made for data entry personnel. The logbook is returned to the analyst and report forms are generated from the LIMS environment.

REPORTING

Sulfide is reported in units of mg/L.

DOCUMENTATION

Documentation must follow the requirements in PEL Laboratories' Quality Manual and SOP00040-QA; *Rules for documentation.*

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff is encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

- *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW*-846 Update III, Method 9030B.
- *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, SW*-846 Update III, Method 9034.
- *Methods for Chemical Analysis of Water and Wastes,* EPA 600/4-79-020, Method 375.4
- SOP G-00041-QA, *Rules for documentation*
- SOP G-00040-QA, *QC activities: numerical data treatment*

PEL Laboratories, Inc.

PEL Laboratories Inc. - Standard Operating Procedure

Sample Analysis: Total Suspended Solids (TSS) (Method EPA 160.2)

APPROVED:

Sample Prep. Section Leader Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. to determine total suspended solids (non-filterable residue) in drinking, surface, and saline waters, domestic and industrial wastes. The filtrate from this method may be used for TDS (filterable residue).

The practical range of the determination is 4 mg/L to 20,000 mg/L.

Residue, non-filterable (TSS) is defined as those solids that are retained by a glass fiber filter and dried to constant weight at 103-105°C.

Non-representative particulates such as leaves, sticks, fish, lumps of fecal material should be excluded from the sample if it is determined that their inclusion is not desired in the final result

Preservation of the sample is not practical. Analysis should begin as soon as possible. Refrigeration or icing to 4°C to minimize microbiological decomposition of solids is recommended.

Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

QA/QC REQUIREMENTS

The holding time for this test is seven days from the date of collection.

This SOP was written to conform all the QA/QC criteria described in the following method: EPA 160.2

For TSS analyses, the following control samples should be run with each batch of samples. A batch is defined as 20 field samples or 18 field samples for AFCEE:

1. Method Blank: Must be run after every 10 samples, to determine if there is any carry over in the batch or other types of contamination within the system.

2. Laboratory Control Sample (LCS): A solution prepared with a known mass from a traceable source is filtered as an LCS. LCS data is entered into a spreadsheet. Concentration determined is entered and the % recovery calculated. When the LCS recovery is outside the range of 80 - 120%, the system must be checked, a new LCS sample is filtered, and the associated blank and batch are re-analyzed. Any out of control event that references client data must be documented in the case narrative (level II, III, IV package) and/or a CAR form.

3. Sample Duplicates: Sample duplicates are run at a frequency of 1 per batch. An RPD greater than 20% is considered outside acceptance limits. When an RPD exceeds 20%, the system is investigated. The problem is corrected when possible, and the measurement repeated. Any out of control event that references client data must be documented in the case narrative (level II, III, IV package) and/or a CAR form.

EQUIPMENT/APPARATUS

1. Glass fiber filter disks, without organic binder, such as Millipore AP-40, Whatman 934AH, Gelman type A/E, or equivalent.
2. Filter support: filtering apparatus with reservoir and a coarse (40-60 microns) fritted disk as a filter support.
3. Suction flask
4. Drying oven, 103-105°C
5. Desiccator
6. Analytical balance capable of weighing to 0.1 mg
7. Tongs.
8. Aluminum weighing dishes.
9. Forceps.
10. Class A 100 mL graduated cylinder.

REAGENTS

Not Applicable

PROCEDURE

1. Preparation of glass fiber filter disk:
   a. Insert the glass fiber filter (47mm) into the bottom of the filter apparatus with the wrinkled surface up.
   b. While vacuum is applied, wash the disk with three successive 10 mL volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through.
   c. Remove filter and place in aluminum weighing dish. Samples should be dried in the oven at 103-105°C for a minimum of two hours. Place samples in desiccator and store until needed.
   d. Weigh filter and dish immediately before use, then record weight in TSS Logbook. After weighing, handle the filter and dish with forceps or tongs only.
2. Place weighed filter in filtering apparatus
3. Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.
4. Shake the sample vigorously and quantitatively transfer the predetermined sample volume to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.
5. Filter 100 mL of sample. Sample size can be decreased for samples with high solid content. (Stop filtering and measure volume filtered when apparatus becomes clogged.)
6. With the suction on, wash the graduated cylinder, filter, residue, and filter funnel wall with three successive 10mL volumes of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.
7. Carefully remove filter from the filtering apparatus and place it back in the aluminum weighing dish. Dry at least 1 hour at 103-105°C. Cool in a desiccator and weigh.
8. Repeat the drying cycle until a constant weight is obtained (i.e. weight loss is less than 0.5 mg). Results are recorded in TSS Logbook.

CALCULATIONS

Equation 1. Calculation of TSS mg/L in Sample

$$TSS = \frac{(A-B)*1000}{C}$$

A = weight of filter and dish + residue in mg
B = weight of filter and dish in mg
C = ml of sampled filtered

REVIEW/VALIDATION

Data review and validation must be reviewed by the section supervisor according to PEL Laboratories, Inc. Quality Manual. After the data review process has been completed, copies of the data logbook are made for data entry personnel. The logbook is returned to the analyst and report forms are generated from the LIMS environment.

REPORTING

TSS (non-filterable residue) is reported in units of mg/L.

Values below 4 mg/L are reported as < 4 mg/L.

DOCUMENTATION

Documentation must follow the requirements in PEL Laboratory's Quality Manual SOP00040-QA; *Rules for Documentation.*

HEALTH AND SAFETY

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staffs are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

- Methods for Chemical Analysis Water and Wastes, USEPA, PB84-128677, March 1983, Method 160.2
- Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989, Method 2540D.

PEL Laboratories, Inc.

PEL Laboratories, Inc. - Standard Operating Procedure

Analysis of Aqueous and Soil Samples for Diesel Range Organics by Gas Chromatography by Method 8015 Modified.

APPROVED:

Section Manager Date

QA Officer Date

Laboratory Director Date

SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the procedures used by PEL Laboratories, Inc. to measure the concentration of diesel range compounds in water, sludge, and soil samples in the alkane range of C10- C28 using baseline-baseline integration.

This SOP is based on a solvent extraction, gas chromatography (GC) procedure. A known amount of sample is spiked with a surrogate and extracted with methylene chloride by the 3510, 3550, or 3580 extraction method. The extract is concentrated to a final volume of 1 ml. A 2 μl aliquot is injected on a capillary column gas chromatograph (GC) equipped with a flame ionization detector (FID). Quantitation is based on the detector response compared to a series of normal alkane standards.

Dilutions should be performed as necessary to put the chromatographic envelope within the instrument linear calibration range.

This SOP should be used by, or under supervision of, analysts experienced in the use of solvent extractions and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool. Staff members performing the procedures described in this SOP are responsible for reading, understanding, and complying with the SOP's requirements. Supervisors are responsible for supplying a copy of the SOP to the analyst, and providing adequate explanation of the material contained.

QA/QC REQUIREMENTS

1. Water samples shall be acidified to a pH of less than 2 with hydrochloric or sulfuric acid (reagent grade or better) when collected. The pH should be checked and documented at the time of extraction.
2. The samples shall be stored at 4°C from the time of collection until extraction.
3. Extraction shall be performed on waters within seven days of sample collection and on soils within 14 days of sample collection.
4. All analysis must take place within 40 days of extraction.
5. Initially the following requirements must be met.

- Method Detection Limits, MDLs (must be repeated every 12 months) - A minimum of seven samples are prepared. The samples are analyzed within a valid analytical sequence. The validated detection limit is calculated by multiplying the standard deviation of the replicate results by 3.14. In addition, the average recovery from the MDL replicates should be between 70% and 130% of the true value. Reporting limits are valid only if they are greater than or equal to the validated method detection limit values. Standard reporting limits can be any convenient value that meets the above criterion, but are typically equal to the lowest calibration level. However, the report limit for each target must be reconsidered for every sample by viewing the chromatogram and associated quantitation report.

6. Four replicates - Method performance validation is performed by analyzing at least four replicate spiked water samples. To establish initial method precision and accuracy, calculate mean % recovery and percent relative standard deviation (RSD) of each target compound.

7. The following procedures will be used to demonstrate that the system is in control on an on-going basis. Applicable ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

- Instrument blanks - The analyst will analyze an instrument blank to demonstrate that interferences from the analytical system are under control every twenty four hours. The instrument blank is methylene chloride. The instrument blank is considered to be interference-free when targets are not detected above the method detection limit.
- Method blank - The analyst will analyze a method blank to demonstrate that interferences from the prep and analytical system are under control every twenty samples or per analytical batch, whichever is more frequent. The method blank is processed through the same procedure as the samples and can have no targets above the report limit. Blank water and Ottawa sand are used for laboratory method blanks.
- Other blanks - Trip, equipment, and field blanks are provided by the client to monitor contamination during sampling and shipping. These types of blanks are treated and reported as regular samples.
- Second Source Standard - The analyst will analyze a second source standard minimally once per calibration to demonstrate that the operation of the measurement system is in control and must be +/- 20% D.
- Surrogates - Surrogates are added to all samples (including QC samples) immediately before extraction to monitor sample preparation efficiency. Poor surrogate recovery requires investigation. Re-extraction is the logical corrective action if sufficient raw sample is available and if the holding time has not expired. If recoveries are outside established limits, 70%-130%, verify calculations, dilutions, standard solutions and instrument performance. High recoveries may be due to a coeluting matrix interference or the presence of high molecular weight contaminants; examine the sample chromatograph. High recoveries may also be due to memory effects caused by poor sample volatility, backflash or carryover. Check instrument conditions, injection volume and injector temperature. Low recoveries may be due to adsorption by the sample matrix. Low recoveries may also be caused by incorrect integration. If the surrogate recovery is outside of established limits, the results must be flagged and an explanation offered.
- Matrix spike/Matrix spike duplicate (MS/MSD) - At least every 20 samples or once per prep batch (whichever is more frequent), an aliquot of an environmental sample is spiked with known quantities of the method analytes. The MS/MSD is analyzed exactly like a sample, and its purpose is to determine whether sample matrix contributes bias to the analytical results by determining the accuracy of each and the precision associated with the spikes. The background concentrations of the analytes in the native sample must be determined in a separate aliquot and the measured values in the MS/MSD corrected for native concentration. If the client has not identified samples to be spiked, the laboratory will randomly choose non-QC samples for spiking. A reagent blank is also spiked and duplicated and may be used for QC reporting in the event matrix interference causes the sample MS/MSD to fail.

MS/MSD	
% Recovery Limits	% RPD
70-130	0-30

- LCS (Blank spike) - Target compounds are spiked into laboratory blank matrix (reagent water or Ottawa sand). LCS is especially useful to demonstrate that the system is in control, even when MS/MSD do not meet criteria. It is also useful to determine if poor performance in the MS/MSD may be attributed to matrix effects. The calculated spike recovery shall be used as a control and should be between 70%-130%.

- Instrument Performance - The performance of the entire analytical system is monitored by evaluating data gathered from analyses of laboratory method blanks, standards, and samples. Significant peak tailing of the target compounds should be corrected. Tailing problems are generally traceable to active sites in the GC inlet, on the GC column, improper column installation, or problems with the operation of the detector.

- Initial and continuing calibration will be performed on an on-going basis as described in the calibration section of this SOP.

8. When any of the above criteria is not achieved, the analyst must repeat the test only for that analyte which failed to meet criteria. Repeated failure will confirm a general problem with the measurement system or faulty samples and/or standards. If this occurs, locate and correct the source of the problem and repeat the test.

EQUIPMENT/APPARATUS

1. Gas chromatograph (HP 5890 Series II) using an FID monitored by a HP Vectra XM computer with Target software for data processing. A HP Laserjet printer is used to print reports.
2. Capillary column- 30m X 0.53 mm ID-(Restek part # 10270)
3. HP 7673 Automatic Injector with a 10 µl syringe (HP part # 5181-1267)
4. FID jet tip (HP catalog # 19244-80560)
5. Methylene Chloride: B&J brand
6. Top level stock standard mixes: Prepare primary standard from commercially obtained diesel fuel. Preparation of all standards should be documented in the semi-volatile standards logbook. Stock standard solutions must be replaced after 1 year, or sooner if comparison with secondary check standards indicate a problem.
7. A secondary source standard is prepared at 300 µg/ml or total range at 2.4 mg/L (Restek).
8. Each sample, reagent water blank, and quality control check is spiked with OTP (Ultra catalog #IST-480). The concentration level of OTP must remain constant in the standards at 100 µg/ml.

REAGENTS

1. Methylene chloride - pesticide grade or equivalent.
2. Recommended Surrogate Spiking Solution: Ortho-Terphenyl (OTP). A working solution is made at 100 µg/mL in methanol. To be added to all samples and quality control samples before extraction and to the standards
3. Target spiking solution - A working solution of Petroleum Hydrocarbon standard (C10 – C28).
4. Components in Petroleum Hydrocarbon Standard:

Decane	C_{10}
Dodecane	C_{12}
Tetradecane	C_{14}
Hexadecane	C_{16}
Octadecane	C_{18}
Eicosane	C_{20}
Docosane	C_{22}
Tetracosane	C_{24}
Hexacosane	C_{26}
Octacosane	C_{28}

INTERFERENCES

1. Other organic compounds, including chlorinated hydrocarbons, phenols, and phthalate esters are measurable.
2. High purity reagents (Burdick & Jackson) must be used to minimize interference problems.

3. Method interferences are reduced by washing all glassware with hot soapy water followed by successive rinses with tap water, acetone, and methylene chloride. At least one reagent blank must be analyzed with each batch or for every 20 samples to demonstrate that the samples are free from method interference.
4. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of an instrument blank to check for instrument contamination.
5. The extent of matrix interference will vary considerably from sample to sample.

PROCEDURES

1. Method Calibration

Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with methylene chloride. PEL uses levels of 500, 400, 300, 200, and 100, and 50 μg/ml for each compound. This is equivalent to 4 mg/L, 3.2 mg/L, 2.4 mg/L, 1.6 mg/L, 0.8 mg/L, and 0.4 mg/L respectively for total petroleum hydrocarbons (total peak area). If the %RSD for the initial calibration is more than 20%, the curve needs reanalyzed and/or remade. Calibration standards must be replaced after six months, or sooner if comparison with check standards indicate a problem.

The working calibration curve must be verified on each working day by one or more working standards. If the %D for the continuing calibration standard is more than $\pm$ 15%, the test must be repeated using a fresh calibration standard, or an entire new curve must be prepared.

2. Analytical

Sample preparation must be done by one of the following methods:

Matrix	Methods
Water	3510
Soil/Sediment	3550
Waste	3550, 3580

3. The recommended GC/FID operating conditions:

Injection temperature:	280°C
Detector B temperature:	300°C
Initial column temperature:	60°C, hold for 3 min.
EPC column temperature program:	Ramp to 300°C at 20°C/min.
Final column temperature:	300°C
Sample volume:	2μl
Carrier gas:	Helium
Pressure:	6.0 psi
Run time:	25 min.

Performance Criteria: GC run conditions and columns must be chosen to meet the following criteria:

The column must be capable of separating typical petroleum hydrocarbon components from the surrogates.

4. Retention Time Window Definition- Before establishing windows, be certain that the GC system is within optimum operating conditions. Make three injections of the method standard throughout the course of a 72 hour period. Serial injections over less than a 72 hour period result in retention time windows that are too tight.

   Calculate the standard deviation of the absolute retention times for the surrogate, C10, and C28.

   The retention time window for individual peaks is defined as a plus or minus three times the standard deviation of the absolute retention time for each component.

   Retention Time Window - The retention time window for the surrogate and C10 and C28 shall be within the established range. If they are out of acceptance range, a new initial calibration must be prepared and verified before samples are analyzed.

   In those cases where the standard deviation for a particular analyte is zero, the laboratory will use the window of a nearby peak.

QUALITY CONTROL

1. Analytical Sequence

   a. All samples reported to the client must be analyzed within a valid analytical sequence. An analytical sequence is a set of GC acquisitions. It begins with the initial calibration, continues with the analysis of sample extracts bracketed by continuing calibration checks. At a minimum, the initial calibration consists of five levels of calibration standards to demonstrate sensitivity, resolution, and system response as a function of concentration (linearity). The lowest level of the initial calibration standards should be near or at the report limit. If initial calibration criteria are satisfied, then sample extracts may be analyzed. The continuing calibration check must be reanalyzed at the end of the analytical sequence. All samples must be bracketed by successful continuing calibration check standards.
   b. No limit is placed upon the amount of time that an initial calibration may be valid, nor is there a maximum limit on the number of samples associated with one initial calibration. As long as continuing calibration check standards meet continuing calibration criteria, then the initial calibration remains valid.
   c. Minor instrument maintenance is permitted to achieve successful continuing calibration checks. Minor instrument maintenance includes replacing injection port septum, cleaning or replacing injection port liner.
   d. The second source standard must be secured from a second vendor. Its purpose is to provide comparison of mid level standards derived from two different sources. If significant difference is observed between the calibration standard and the historical standard, both standards are suspect and further investigation is required to identify an accurate standard.

      Example Analytical Sequence

      Instrument Blank (DCM)
      Instrument Blank (DCM)
      Standard Level 5
      Standard Level 4
      Standard Level 3
      Standard Level 2
      Standard Level 1
      Second Source Standard ±20%
      Instrument Blank
      10 injections
      CCV

2. Initial Calibration

   a. The analytical sequence must begin with a valid initial calibration for each column.

b. The resolution should be adequate so that software algorithms can separate and identify all compounds of interest at **all** concentrations. Poor chromatographic resolution diminishes the evidence for proper peak identification and quantitation. The resolution recommendations are not for target peaks only. Extraneous (system or degradation) peaks should be adequately resolved from target peaks. Percent resolution is calculated by dividing the height of the valley by the height of the smaller peak being resolved, multiplied by 100.

c. The variability of retention times must be assessed according to section 7.5 of Method 8000. At least three injections of each target parameter are required within a 72-hour period. The size of each parameter's search window is three standard deviations of the observed retention times. The search window for each parameter of interest is centered during initial calibration by the mid-level of the calibration curve. Note that the size of the search window is not reestablished at every initial calibration. However, the search window size must be reevaluated following major changes in instrument configuration which might significantly affect the variability of retention times. In those cases where the standard deviation is so small that unacceptably small retention time windows would be calculated, the laboratory may substitute a valid retention time window of a close eluting, similar compound.

d. The initial calibration sequence may begin with an instrument blank (solvent with internal standard) to establish instrument rhythm. This instrument blank will also provide early warning if the analytical system is contaminated. Instrument blanks must not produce false positive signals at or above the method detection limit for any target parameter.

e. Before any compound may be calculated and reported present in a sample, calibration standards containing each analyte of interest must be analyzed at a minimum of five concentration levels. One of the levels should be at or near the method report limit. The other levels should correspond to the expected range on concentrations found in samples. A calibration curve must be developed for each parameter. In order for the curve to be acceptable, the experimental data points for each compound must fall near enough to the calculated curve to provide a coefficient of determination (r^2) of 0.995 or better. If any r^2 value obtained is less than 0.995, corrective action must be taken and documented the curve must be regenerated.

f. Alternatively, calculations may be made using the mean response factor if the linearity of the system through the origin is sufficient to produce less than 25% relative standard deviation of the five response factors. The calibration requirements apply to all compounds that are targets of applicable samples.

g. No limit is placed upon the amount of time that an initial calibration may be valid, nor is there a maximum limit on the number of samples associated with one initial calibration. As long as continuing calibration check standards meet criteria, then the initial calibration remains valid.

3. Continuing Calibration: Samples may be analyzed immediately following a successful initial calibration, but continued good performance must be demonstrated as sample extracts are analyzed. Continuing calibration standards offer a mechanism to monitor small fluctuations in instrument response and ensure that the initial calibration is still valid for sample analysis. For acceptable sustained instrument performance, the continuing calibration checks must meet the following criteria of quality.

4. Sample Analysis

a. If targets exceed the instrument calibration range, the extract must be diluted and reanalyzed. Dilutions should be performed so that the most intense target is within the upper half of the calibration range.

b. Occasionally interferences will persist in the extract. Precise rules for diluting interferences are difficult to develop. A single non-target peak could be allowed to saturate the detector. But some extracts might elevate the baseline or alter the baseline noise for part of the chromatogram. Allowing the baseline to severely elevate or noise to obstruct the target chromatographic region would serve no purpose. Data should be examined promptly so the dilutions, reanalysis, and/or reextraction can be scheduled..

c. The results of all injections that follow a high level sample or sample with late eluting compounds must be c arefully examined for the possibility of crossover.

d. Questionable samples should be reanalyzed.

e. Instrument blanks can be analyzed after suspect samples to evaluate instrument crossover.

f. All chromatographic data requires interpretation. The computer algorithms defined by the acquisition method file (chromatographic method) should be biased to favor false positives. This bias will alert the analyst to potential targets that require consideration and possible further investigation. Interpretation by the analyst should favor false negatives.

g. Peak identification is based upon retention time comparison to recent calibration data. Library retention times are established during initial calibration and the retention time windows are centered. Library times may be updated as frequently as every day thus recentering retention time windows

h. The analyst should not rely exclusively on the quantitation report for qualitative decisions. The experienced analyst must consider all chromatographic features such as peak shape, resolution comparison to surrounding noise. Graphically overlaying the sample and standard chromatograms provides the most selective method of peak identification. The analyst should compare the sample peak(s) to a standard of similar concentration when possible.

i. Computer algorithms normally assign peak start, peak stop and baseline positions within the chromatogram. The acquisition method (chromatographic method) file controls these algorithms. An optimized acquisition method will provide accurate peak detection and integration for most samples. But some extracts will offer unusual chromatographic noise the algorithms may produce inflated peak areas. The analyst must review every chromatogram for accuracy of peak integration. Timed events may be added as needed to the acquisition method file to improve integration.

j. A hard copy of the final quantitation report is always saved with the project folder. This report is the usual place to document comments and manual calculations for review and archival.

5. Data Reduction and Reporting

a. The analyst will review the data pack for completeness and quality. Sometimes it will be necessary to collect more data before reporting sample results.

b. The analyst should develop a consistent/logical procedure for reducing data which can be reviewed and understood by other GC analysts and data reviewers. Generally, data reduction is documented on the "working" quantitation reports that are kept in the project folder. Any special notes, comments or additional data may also be documented and filed in the project folder for archival.

c. If interference prevents the detection of a target the analyst may choose to perform a dilution on the sample, which will in turn raise the reporting limit. Raised report limits should be addressed in the comment field of the Form I and the case narrative for Level III samples.

d. For rounding numbers to the appropriate level of confidence, observe the following common rules. If the figure following those to be retained is less than 5, drop it (round down). If the figure is greater than 5, drop it and increase the last digit to be retained by 1 (round up). If the figure following the last digit to be retained equals 5, round up if the digit to be retained is odd, round down if that digit is even.

e. The report limits must be issued with correction for any extract dilution.

f. The associated QC data for blanks and surrogates should be reported with the sample data. The values obtained for common laboratory contaminants should be reported for both blanks and samples without blank subtraction.

g. Analytical results are summarized from the raw data. Sample results are reported without blank subtraction. The appropriate qualifiers should be used on the Form 1 and discussed in the case narrative. Sample results (confirmed compounds and report limits) should be reported to two significant figures. Three significant figures may be used to express surrogate and spike recoveries over 100 percent.

h. A case narrative must be constructed for all samples within the delivery group (lab batch). Any unusual difficulties experienced with the sample analysis should be documented as a comment on the analytical report and in the case narrative.

i. When data is reduced and final report is ready to be prepared, the analyst should review his/her own work for any errors or inconsistencies. Common errors include, but are not limited to, the following:
   1) Transcription errors.
   2) Corrections for dilutions.
   3) Correct list of targets.
   4) Reporting poorly integrated quantitations.
   5) Appropriate QC reported.

CALCULATIONS

1. An initial calibration curve may be determined and used to calculate any parameter. Calculation from a curve is the preferred method to determine an analyte. Either a linear equation or a quadratic equation may describe the relationship between relative response and relative amount.
   a. For a linear curve: $y = ax + b$

b. For a quadratic curve: $y = ax^2 + bx + c$

c. Alternatively results may be calculated using a single RRF according to the following equation.

$$(Conc_x^{samp}) = \frac{(Area_x^{samp})\,(Area_{IS}^{std})\,(Amt_x^{std})\,(Amt_{IS}^{samp})}{(Area_x^{std})\,(Area_{IS}^{samp})\,(Amt_{IS}^{std})\,(T)\,(P)}$$

Where:
P = Portion (fraction) of extract combined with IS
T = Total raw sample producing total extract

d. Substituting the RRF:

$$Conc_x^{samp} = \frac{(Area_x^{samp})\,(Amt_{IS}^{samp})\,(RRF^{std})}{(Area_{IS}^{samp})\,(T)\,(P)}$$

2. All quantitations (report limits and confirmed targets) for soils, sediments and sludges must be corrected for dry weight (unless client specifies reporting on a wet weight basis.)

a. $D\ (dry\ weight) = \frac{a) - \%moisture}{a)}$

b. $Corrected\ quantitation\ (dry\ result) = \frac{(1)\ \mu g/Kg\ (wet\ result)}{(1)\ D\ (dry\ weight)}$

REVIEW/VALIDATION

All data is first reviewed by the analyst(s) most familiar with the data. This includes but is not limited to the analyst(s) performing the acquisition, data reduction/interpretation, and reporting.

Final review is performed by the section supervisor or designated senior analyst.

All persons reviewing and releasing data must be qualified in gas chromatographic data interpretation as well as specific procedures outlined in this SOP.

The sample data must be reviewed with the associated quality control data. The following items should be checked before reporting sample results (review is not limited to these items).

1. Instrument Blank
2. Valid Initial Calibration
3. Valid Continuing Calibration
4. Acceptable Method Blank
5. Acceptable MS/MSD and Blank Spike (LCS)
6. Acceptable Surrogate Recoveries according to Control Chart Limits
7. Results Corrected for Dilutions
8. Chromatographic Data Integration and Interpretation (evaluate possible crossover, peak shape, retention time, surrounding chemical noise)

CORRECTIVE ACTION

Corrective action procedures are the responsibility of the analyst for out-of-control conditions.

Initial calibration criteria must be met. Failure to pass initial calibration criteria prohibits the analysis of samples. Repeated failure to pass criteria may indicate that instrument maintenance is needed. Instrument blanks which fail criteria requirements should alert the analyst to expect false positive data for any associated samples.

Insufficient instrument sensitivity guarantees that method detection and report limits will not be achieved. When resolution criteria cannot be achieved (i.e. algorithms do not separate and identify all calibration compounds) the algorithms can be adjusted and samples and standards should be reprocessed with the corrected algorithms. Integration parameters necessary to produce final data are saved in the acquisition method file which is documented in the GC injection log book. If criteria cannot be achieved for all components, the analyst should be alerted that the system identifications may not be correct and special evaluation my be required.

Failure to pass continuing calibration criteria requires reanalysis of any affected samples. Repeated failure to pass response factor criteria requires a new initial calibration.

Samples must be diluted properly for analysis. Not diluting a high-level or noisy sample makes data interpretation difficult and very subjective. Over diluting provides unnecessarily high report limits to the client and should be avoided. "Challenging" extracts should be analyzed at the lowest dilution factor which will still provide reliable data interpretation for all petroleum hydrocarbon ranges.

The surrogate is spiked into every sample to monitor the success of each preparation. Surrogate and spike recoveries will occasionally exceed control limits. Unusual recoveries must be investigated.

1. Check for errors in the calculation. Inspect the chromatogram for poor integration or interference with either the surrogate or spike peak and the internal standard. Check the primary and confirmation data (when available) for consistency.
2. A surrogate recovery higher than the control chart limits may be caused by a double fortification of the surrogate solution during sample extraction. Check sample documentation.
3. Check for documented problems during sample extraction or cleanup.
4. Check instrument performance and reanalyze the extract if appropriate.
5. The sample may be reextracted if adequate raw sample is available. Both extractions are usually reported if the reextraction is performed beyond holding time.

Any investigations and results should be documented in the project folder and if necessary explained in the case narrative for Level III projects.

DOCUMENTATION

Preparation of the sample extract is documented in a bound extraction logbook. A copy of the extraction log is included with the queue list.

Each GC has its own bound maintenance journal. This journal contains records of instrument maintenance, repair, and modifications. Each entry will be dated and signed by the analyst.

Each GC has its own bound sample injection log book. All initial calibration, continuing calibration, and sample injections are entered. Each entry contains the run number (file name), date, and sample identification. The raw data files and acquisition method files are archived onto CD and then deleted from the hard disk after review is complete.

HEALTH AND SAFETY

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available.

Any unfamiliar water sample may offer dangerous contents beyond the list of chemicals listed in this SOP. All samples and extracts should be treated as potential health hazards and handled with proper precautions.

Appropriate protective equipment and clothing must be used under the assumption that all samples are potentially hazardous. Safety glasses, gloves and lab coats are a minimum requirement. The persistent presence of noxious odors may be indicative of failure of the laboratory ventilation system and must be reported to a supervisor or manager.

Laboratory staff are encouraged to review the Chemical Hygiene Plan for general safety policies, and Material Safety Data Sheets for reagents used in the laboratory.

REFERENCES

- Guidance for the Preparation of Standard Operating Procedures for Quality-Related Documents, EPA QA/G-6, November 1995.

- Method for Determination of Diesel Range Organics. Developed from: SW-846 Methods 8000 and 8100; Method OA-2; and work by the EPA Total Petroleum Hydrocarbons Methods Committee.

- State of California. Leaking Underground Fuel Tank Field Manual: Guidelines for site assessment, cleanup, and underground storage tank closure, 1989.

DRO Standards Preparation

Analyte/Mix	Vendor	Catalog Number	Concentration in µg/ml
Diesel #2	Circle K gas station	N/A	10,000
Ortho-terphenyl	NSI		

The following DRO standards are prepared in µg/ml: 500, 400, 300, 200, 100, 50.

A working DRO intermediate is prepared from pure commercial diesel fuel. A 1 g sample is weighed on an analytical balance and brought to 100 ml in methanol.

A 1 ml aliquot is taken from this 10 mg/ml mixture and brought to 10 ml again in methanol, creating a working DRO standard at 1000 µg/ml.

ANALYTICAL METHOD

AM15.01G

ANALYSIS OF DISSOLVED GASES IN WATER

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ANALYTICAL METHOD AM15.01G

ANALYSIS OF DISSOLVED GASES IN WATER

1.0 Scope and Application

1.1 Method AM15.01 may be used to determine the concentration of dissolved gases in water samples. Specifically, Method AM15.01 is used to determine the dissolved concentration of the permanent gases.

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in sample preparation, the operation of gas chromatographs and in the interpretation of chromatograms.

2.0 Summary of Method

2.1 Analysis of the permanent gases in a water sample is accomplished by transferring the sample plus helium into a syringe. After equilibration, the headspace gases are analyzed with a gas chromatograph. The sample is introduced into the columns by injection. The data is transferred to a microcomputer where it is converted to digital format, stored, and processed.

3.0 Interferences

3.1 The most likely source of "interference" is ambient air. Due to the relatively high concentrations of oxygen and nitrogen, a very small amount of air will seriously skew the results.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are analyzed.

3.3 The analyst should demonstrate the absence of carryover contamination. This demonstration should be performed prior to the analysis of a sample when carryover contamination is suspected.

3.4 Extra peaks in a chromatogram can be actual peaks from a previous run. Contamination from late eluting peaks can occur between successive injections.

3.5 The analyst should be certain that all peaks have eluted from the previous analysis prior to analyzing any sample or standard. If samples or standard chromatograms contain suspected 'extra peaks' the sample should again be analyzed after a clean baseline is established.

4.0 Apparatus and Materials

4.1 Sample vials: 40 ml VOA glass vials.

4.2 Septa.

4.3 Syringe: Hamilton locking gas tight.

4.4 Gas Chromatograph

4.5 Data Collector

5.0 Sample Preparation and Analysis

5.1 Remove the sample (VOA) vials from the refrigerator.

5.2 Using a clean syringe, withdraw the sample.

5.3 Withdraw a aliquot of helium from a reservoir and lock the syringe.

5.4 Shake the syringe by hand.

5.5 Slowly inject the sample into the gas chromatograph.

6.0 Calibration and Results

6.1 The standard calibration gas should be introduced in the same manner as samples. Measured peak areas are converted to concentrations in percent by volume using certified commercial gas standards traceable to NIST standards. Dilutes may be made to achieve multi point calibration curves.

6.2 At the beginning of a project or sample set, standards of appropriate calibration ranges will be run at least three times.

6.3 The instrument response must not vary by more than 20%.

6.4 Concentration of analytes in the headspace gas in percent by volume are converted to the original analyte concentration in the water (mg/l).

7.0 Quality Control

7.1 If the parameters set forth in section 6.3 are not met, the analytical program will be terminated until the cause is determined and a solution is effected.

7.2 The analyst should demonstrate the absence of ambient air in

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EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613, 8290 AND 551

TLI SOP No.	DSP161 Version: 16	Effective Date:	October 23, 1998
Author:	Phil Albro	Date Written:	October 2, 1998
Authorization: Phil Albro (Management)		Date Authorized:	10/18/98

I. **SCOPE AND APPLICATION:** This SOP provides procedures for the extraction of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran (PCDD and PCDF) from water samples in accordance with methods 1613 or 8290. It may also be applied to the extraction of tetrachlorodibenzo-p-dioxins and tetrachlorodibenzofuran from water in accordance with method 551. See the SOP on Preparation for Extraction of PCDD/PCDF from Water before using the present SOP.

II. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear, and gloves. These solvents are flammable; avoid flames and sparks. Do not breathe the vapors, and avoid contact with skin and eyes. They may cause irritation, nausea, dizziness, and, in extreme cases, death. For additional safety and health information, see the TLI Safety and Health Manual and the appropriate MSDS.

III. **REAGENTS:**

A. Organic-free reagent water- Either Dracor or Fisher HPLC Grade

B. Heptane-pesticide grade or better quality, less than 1 ppm residue on evaporation.

C. Sodium sulfate-anhydrous, pesticide grade.

D. Methylene Chloride-pesticide grade or better quality.

E. Toluene-pesticide grade or better quality.

EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
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IV. GLASSWARE PREPARATION:

A. All glassware used in this procedure must have been prepared according to the SOP entitled "Glassware Cleaning".

B. The following glassware is needed for each sample:

2 L separatory funnel with stopper and Teflon© stopcock

A. 1000 mL graduated cylinder

medium glass powder funnel

250 mL round bottom flask

500 mL extraction flask and regular thimble holder (pre-Soxlet extracted).

Soxlet extractor (pre-Soxlet extracted).

Soxhlet Dean-Stark (SDS) extractor - pre-soxhlet extracted and ready for use

A. Assemble the separatory funnel(s) with stopcock and stopper.

B. Rinse the following with heptane:

separatory funnel(s)

graduated cylinder(s)

all flasks

glass powder funnel(s)

A. While rinsing the separatory funnel(s), close the stopcock and check for leaks. Drain the funnel into a waste container.

B. After rinsing, invert all flasks and allow to fully drain.

EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
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C. Plug the powder funnel(s) with pre-cleaned glasswool. Fill the powder funnel 3/4 full with anhydrous sodium sulfate.

I. SEPARATORY FUNNEL EXTRACTION PROCEDURE:

A. If has not already been done in the preparation of the sample for extraction, pour the sample volume into a 2 L separatory funnel. Rinse the sample bottle with 60 mL of methylene chloride and transfer to the separatory funnel.

B. Extract the aqueous phase with methylene chloride as follows:

1. Shake the separatory funnel with water sample and methylene chloride for 5 minutes using Glas-Col Automatic Shaker (or 2 minutes by hand). Be sure to vent the funnel periodically to avoid pressure buildup.

Note: If using the Gas-Col shaker, set the timer for 5 minutes and turn the power on. Slowly increase the speed to 40 or the maximum speed possible without displacing any sample through the vent.

Allow the solvent layers to settle for 10 minutes. If emulsions occur, filter the water + emulsion through a G8 filter or glass wool with a methylene chloride rinse. Add the methylene chloride rinses to the methylene chloride extract.

2. Drain the methylene chloride layer through anhydrous sodium sulfate into a 250 mL flask.

3. Repeat steps 1-3 two more times using 60 mL methylene chloride for each extraction. A total of three extractions are required for each sample.

1. Rinse the sodium sulfate twice with 10 mL methylene chloride. Collect the methylene chloride rinses in the 250 mL flask containing the sample extract.

I. EXTRACTING THE FILTER:

A. Soxhlet extract the filters, glasswool used to break emulsions, and all filtered solids as follows:

EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

1. Place filters in a toluene pre-Soxhlet extracted thimble (500 mL size).

2. For methods 1613 and 8290, add 375-400 mL of toluene to the 500 mL boiling flask; For method 551, use 400 mL of ethanol: toluene 68:32 (v/v) to the 500 mL flask.

3. Add 5-6 Teflon boiling chips to the boiling flask.

4. Place the label containing information for the concentration process on the boiling flask on top of colored lab tape. Write solvent used on flask with marker.

a) Do not place set up on hotplates until extraction of the water phase is completed to insure no additional emulsions need to be filtered and the filter or glasswool placed into the thimble with the first filter.

2. Extract using pre-Soxhlet extracted Soxhlet apparatus for 16 hours.

3. After extraction, let cool and ensure the label indicating that this extract is to be combined with the methylene chloride extract from the water phase is still intact.

II. CONTINUOUS LIQUID-LIQUID EXTRACTION PROCEDURE:

Note: The use of the continuous liquid-liquid extractor is always allowed as an alternative to separatory funnel extraction in method 8290. It is the technique of choice when a given sample type is known to produce difficult emulsions. Use this technique with methods 1613 (A or B) and 551 whenever a re-extraction is needed because of low recoveries during the separatory funnel extraction step. Be sure to indicate on the extraction form whenever L-L extraction was used.

Note 2: The L-L extractor simply substitutes for a separatory funnel; therefore all considerations of filtering, determination of solids or particulate solids, or water vs. sludge described in the SOP on Preparation for Extraction of PCDD/PCDF from Water for Methods 1613, 8290 and 551 still apply.

EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

A. Assemble Glassware

1. Using pre-extracted glassware, rinse the extractor body and 500 mL flat bottom flask with methylene chloride. Discard rinse as waste.

2. Place 5-6 methylene chloride pre-extracted boiling chips in the flat bottom flask. Add approximately 250 mL of clean methylene chloride to the flask.

3. Add approximately 150 mL of methylene chloride to the extractor body.

4. Attach extractor body to the flask with green plastic clamp.

5. Label flat bottom with solvent, project number and sample number using color labels.

B. Preparation of Water Sample

1. Measure and record 1 liter of Reagent water each for blank and either OPR (1613), or LCS/LCSD (8290) utilizing a 1000 mL graduated cylinder.

2. Measure 1000 mL of well mixed sample and transfer to the extractor body. Record this volume on the sample preparation and tracking form. Note: If the sample does not contain 1000 mL, record the volume it does contain, but make up the difference with Reagent water. The L-L apparatus needs 1000 mL of water to operate correctly. The sample size to use in calculations, however, is the actual sample size not including make-up water.

3. Rinse the 1000 mL graduated cylinder three times with 20 mL methylene chloride and transfer rinses to the extractor body.

C. Extraction

1. Place Continuous Liquid-Liquid setup on condenser/hot plate and seat securely in place. Use aluminum foil shimmies to align body vertically and to fill any space between hotplate and bottom of the flask.

EXTRACTION OF PCDD/PCDF FROM WATER FOR METHODS 1613A 8290 AND 551	
TLI SOP No. DSP161 Version: 16	Date Written: October 2, 1998

2. Turn hotplate on to 400 degrees.

3. Extract for 18 hours.

4. Dismantle setup after they have cooled. Keep only the methylene chloride in the flat bottom flask.

5. Discard water and methylene chloride in extractor body as waste.

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EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290

TLI SOP No.	DSP105 Version: 15	Effective Date:	July 31, 1998
Author:	Don Harvan	Date Written:	May 4, 1998
Authorization:	Phil Abbo (Management)	Date Authorized:	5/27/98

I. **SCOPE AND APPLICATION:** This method provides procedures for the extraction of polychlorinated dibenzo-p-dioxin (tetra- through octachlorinated homologues; PCDDs) and polychlorinated dibenzofuran (tetra- through octachlorinated homologues; PCDFs) from non-tissue solids, including but not limited to soil, sediment, pulp, sludge, paper and/or cardboard, according to SW-846 Method 8290. Only the extraction procedure is contained in this SOP.

II. **SAFETY CONSIDERATIONS:** Samples may contain harmful substances. Wear labcoat, appropriate eyewear and gloves. Toluene and ethanol are flammable; avoid flames and sparks. The procedure has been validated for either heptane or hexane, since heptane is much less of a health hazard, it should be used instead of hexane whenever possible, but hexane can be used if heptane is unavailable. Do not breathe the vapors, and avoid contact with skin or eyes, as these solvents may cause irritation, nausea, and dizziness. For additional safety information, see the TLI Safety and Health Manual and the appropriate MSDS.

NOTES: **Slight procedural differences exist for specified sample types in this SOP. Be careful not to overlook these differences.**

III. **REAGENTS:**

A. Heptane- pesticide grade (< 1 ppm residue)

B. Toluene- pesticide grade (< 1 ppm residue)

C. Ethanol- OmnySolve grade

D. Ethanol/toluene (68/32 v/v) - Take 68 parts (by volume) of Ethanol and mix well with 32 parts (by volume) of Toluene.

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
TLI SOP No. DSP105 Version: 15	Date Written: May 4, 1998

IV. GLASSWARE PREPARATION

A. All glassware used in this procedure must have been prepared according to glassware washing SOP.

B. The following glassware is needed for each sample:

1. beaker
2. 500 mL or 250 mL flat bottom flask
3. forceps
4. spatula
5. thimble holder - pre-Soxhlet extracted and ready to use
6. Soxhlet extractor - pre-Soxhlet extracted and ready to use

C. If wet sample ≥ 15 g, Soxhlet Dean Stark (SDS) extractor must be used in addition to the Soxhlet extractor. Be sure the SDS extractor has been pre-Soxhlet extracted.

D. The flask, thimble holder and Soxhlet or SDS extractor may be 250 or 500 mL, but all pieces must be the same size.

E. If SDS is required, assemble the SDS extractor with stopcock.

F. Rinse all glassware with n-heptane.

G. Label each beaker and flask by placing a color coded sample label on top of a strip of colored lab tape. The colored lab tape is necessary because the adhesive on the color coded labels is difficult to remove from the glass and will cause contamination problems.

H. All flasks require two labels - one on the side of the flask and one on the neck.

V. EXTRACTION PROCEDURE:

A. Plan the extraction batch. An extraction batch can contain up to twenty (20) samples and must include a method blank, a spike pair, and at least one(1) Lab

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
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Control Spike (LCS). Complete the QC batch form, including all samples and QC samples in the extraction batch.

B. Observe and document the physical appearance and consistency of each sample in the wet lab observation log in MILES.

C. Using the percent moisture analysis, determine the amount of sample necessary for a 10 g dry weight sample.

Note: Mix the sample well before taking an aliquot for extraction.

D. For each sample, weigh the amount of sample determined in step VI.C. above. Record the sample weight on the Sample Preparation Management and Tracking Form (SPMFT).

E. Make sure homogeneity is maintained--exclude anything that does not constitute sample's natural matrix.

F. Clean balance by swiping with heptane.

G. Zero balance. Weigh sample and its container.

H. Record the gross weight on the STMF (Sample Tracking and Management Form).

I. Tare beaker in which sample is to be transferred.

J. Record the sample weight on the STMF (Sample Tracking and Management Form). Also indicate with the letter"Y" or "N" if all the sample was used.

(Y)=There is enough sample left to perform re-extraction
(N)=There is NOT enough sample left to perform re-extraction

K. Reweigh sample and its container weight. Record the post-gross weight.

L. Prepare the blank using pre-extracted G-8 filters for pulps and all dried and ground samples. Prepare the blank using pre-extracted sand for all normal ash/sediment/soil/sludge samples. If any laboratory control samples (LCS and/or

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
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LCSD) are included in the batch, use the same matrix as Blank. Weigh out 10 grams (± 0.4) for each blank and/or OPR prepared.

M. Check the volume of each standard solution relative to the last volume mark. The bottom of the meniscus must be at the mark.

N. Spike all samples with 20 µL USF-I (0.1µg/mL). Spike any Lab Control Spikes,(LCS/LCSD), Matrix Spikes (MS/MSD) with 40 µL USF-MX (0.01 µg/mL). Record the volume, lot number, concentration and expiration date of each standard on the SPMFT and initial and date the entry. At the end of the spiking process, mark the bottom of the meniscus with a fine point permanent marking pen. Return the standard vials to the storage drawer.

Note: Dioxin standards must be stored at room temperature in amber, glass vials, with Teflon lined septa caps. Spiking instructions can be found in See SOP on Concentration of Extracts Using Rotary Evaporator.

O. After spiking place a glass wool plug on top of the sample in each thimble. Use pre-extracted glasswool.

P. Prepare the Soxhlet apparatus by:

1. Use a 500 mL setup, place 400 mL toluene* in the flatbottom flask. Add 5-6 Teflon boiling chips in each flask.
2. Place the label containing information for the concentration process on the boiling flask on top of the colored lab tape. Write the solvent used on the flask.
3. Place the pre-Soxhleted thimble holder on top of the flask.

Q. ***NOTE:** GP pulp sludge samples require 68:32 ethanol/toluene instead of toluene. GP pulp samples require ethanol instead of toluene. The volume remains 400 mL for 500 mL setup.

R. Place the thimble with the spike sample into the thimble holder. Be sure to seat the thimble at the bottom of the holder.

S. **NOTE:** While the Soxhlet apparatus is sitting on the counter, keep the top capped with aluminum foil to avoid contamination.

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T. Place the Soxhlet on top of the thimble holder. If Soxhlet Dean Stark (SDS) is being used, be sure the stopcock is closed.

U. Place the Soxhlet apparatus on the heating mantle and connect the Soxhlet apparatus to the condenser at the ground glass joint. Cap the top of the condenser with aluminum foil.

V. Wrap the thimble holder and Soxhlet extractor with foil. Do not cover the condenser.

W. **NOTE:** If using ethanol as the sole solvent, do not wrap any of the apparatus with aluminum foil.

X. Place a piece of colored tape on the condenser to indicate it is being used for a sample and needs to be pre-Soxhlet extracted after the sample extraction is completed.

Y. If the samples have been designated **high level** write **2X** on the tape. If samples have designated **Isolation** write **3X** on the tape.

Z. Turn on the heat. If using a hot plate, use the heat setting #5. If using a six (6) place mantle, use the HIGH setting.

AA. Check the units after one (1) hour. Each unit should be cycling at a rate of five (5) times per hour, have no leaks and have sufficient solvent. Open the aluminum foil on the thimble holder to check the cycling action and close the wrapping. Make adjustments as necessary.

BB. If adjustments were required, check the units again in one (1) hour. Otherwise check again in six (6) hours.

CC. If the weighed sample is >30g, drain the water from the SDS halfway through the extraction (i.e., approximately 8 hours after turning on the heaters).

DD. Extract the sample for 16 hours.

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EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290

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Dioxin Sample Preparation Tracking & Management Form

Project: 91300 Client: Triangle Laboratories, Inc. (TLI01)

Solvent(s)/Acid(s): _____ / _____ / _____ Method: 8290X:Tetra-octa Matrix: _____

Lot Numbers: _____ / _____ / _____ Extraction Date: __/__/__

IS Spike: 20 µl conc: 0.1000 ng/µl
SS Spike: ___ µl conc: __.____ ng/µl
MB Spike: 0 µl conc: 0.0000 ng/µl
LCS Spike: 0 µl conc: 0.0000 ng/µl

						_____	_____	_____	_____
						_____	_____	_____	_____
						_____	_____	_____	_____
						__ / __ /__	__ / __ /__	__ / __ /__	__ / __ /__
						__ / __ /__	__ / __ /__	__ / __ /__	__ / __ /__
	TLI /		GROSS	SAMPLE		___ : ___	___ : ___	___ : ___	___ : ___
SS.crd	SAMPLE /	CLIENT	WEIGHT	SIZE		_____ng/µl	_____ng/µl	_____ng/µl	_____ng/µl
	ID /	SAMPLE ID	Before After	g / ml		_____ µl	_____ µl	_____ µl	_____ µl
	TLI Blank								Any Left:
000	TLI Method Blank								yes/no
									Any Left:
									yes/no
									Any Left:
									yes/no
									Any Left:
									yes/no
									Any Left:
									yes/no
									Any Left:
									yes/no
									Any Left:
									yes/no
									Any Left:
									yes/no
									Any Left:
									yes/no

Gross weight of sample container - sample before/after aliquot removal.

Comments: _____

_____

_____

_____ Initials: _____ Date: __/__/__

Initials of both SPIKER AND OBSERVER must be entered. XXXXX - Gross weight not provided for WATER Samples.

REV 05/27/97 (FSTM 71)

ATTACHMENT 1

EXTRACTION OF PCDD/PCDF FROM SOLIDS (NOT TISSUE) - 8290	
TLI SOP No. DSP105 Version: -15	Date Written: May 4, 1998

Composition of Fortification Standards

USF-I

Analyte	Concentration (µg/mL)
13C, 2,3,7,8-TCDF	0.1
13C, 2,3,7,8-TCDD	0.1
13C, 1,2,3,7,8-PeCDF	0.1
13C, 1,2,3,7,8-PeCDD	0.1
13C, 1,2,3,6,7,8-HxCDF	0.1
13C, 1,2,3,6,7,8-HxCDD	0.1
13C, 1,2,3,4,6,7,8-HpCDF	0.1
13C, 1,2,3,4,6,7,8-HpCDD	0.1
13C-OCDD	0.2

USF-MX

	Concentration (µg/mL)
3-MonoCDF	0.01
3-MonoCDD	0.01
2,3-DiCDF	0.01
2,3-DiCDD	0.01
2,3,8-TriCDF	0.01
1,2,4-TriCDD	0.01
2,3,7,8-TCDF	0.01
2,3,7,8-TCDD	0.01
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.05
1,2,3,7,8-PeCDD	0.05
1,2,3,4,7,8-HxCDF	0.05
1,2,3,6,7,8-HxCDF	0.05
1,2,3,7,8,9-HxCDF	0.05
2,3,4,6,7,8-HxCDF	0.05
1,2,3,4,7,8-HxCDD	0.05
1,2,3,6,7,8-HxCDD	0.05
1,2,3,7,8,9-HxCDD	0.05
1,2,3,4,6,7,8-HpCDF	0.05
1,2,3,4,7,8,9-HpCDF	0.05
1,2,3,4,6,7,8-HpCDD	0.05
OCDF	0.1
OCDD	0.1

USF-C

Analyte	Concentration (µg/mL)
37Cl- 2,3,7,8-TCDD	0.01

ATTACHMENT 2

Appendix C

Field Standard Operating Procedures

Contents

STANDARD OPERATING PROCEDURES

Field Measurements of pH

I. Purpose

To provide a general guideline for the field measurement of pH in water samples.

II. Scope

Standard field pH determination techniques for use on surface water and groundwater samples.

III. Equipment / Materials

- pH buffer solution for pH 4, 7, and 10
- Deionized water in a squirt bottle
- pH meter
- Combination electrodes
- Beakers
- Solution of HCl
- Glassware that has been washed with soap and water, rinsed twice with hot water, and then rinsed twice with deionized water

IV. Procedures / Guidelines

Procedure

1. Before going into the field:
   a. Check batteries.
   b. Do a quick calibration at pH 7 and 4 to check electrode.
   c. Obtain fresh standard solutions.
2. Calibrate meter using the calibration procedure.
3. Pour sample into a clean beaker.
4. Rinse electrode with deionized water between samples.
5. Immerse electrode in sample solution. Record pH reading.
6. Recheck calibration with pH 7 buffer solution after every five samples.

Decontaminate pH meter before use at each sample location. Rinse probe with distilled water before storage each day. Check meter for battery charge and physical damage each day. Store meter and pH buffer solution in a cool, dry environment.

General

1. When calibrating meter, use pH buffers 4 and 7 for samples with pH < 8, and buffers 7 and 10 for samples with pH > 8. If meter will not read pH 4 or 10, something may be wrong with electrode.
2. Measurement of pH is temperature dependent. Therefore, temperatures of buffers and samples should be within about 2°C. For refrigerated or cool samples, use refrigerated buffers to calibrate pH meter.
3. Weak organic and inorganic salts, oil, and grease interfere with pH measurements. If oil or grease are visible, note this on the data sheet. Clean the electrode with soap and water, and rinse with a 10-percent solution of HCl. Then recalibrate the meter.
4. Following field measurements:
   a. Report any problems.
   b. Compare with previous data.
   c. Clean all dirt off of the meter and from inside the case.
   d. Store electrode in pH 4 buffer solution.
5. Accuracy and precision are dependent on the instrument used. Refer to the manufacturer's manual. Expected accuracy and precision are ± 0.1 pH unit.

V. Attachments

- None.

VI. Key Checks / Items

- Check batteries.
- Calibrate.

VII. Preventive Maintenance

- Refer to operation manual for recommended maintenance.
- Check batteries. Have a replacement set on hand.

STANDARD OPERATING PROCEDURES

Field Measurement of Specific Conductivity and Temperature of Water

I. Purpose

To provide a general guideline for the field measurement of conductivity and temperature.

II. Scope

Field instruments must be calibrated daily before beginning sampling activities. The methods and frequencies of calibration for the instruments used for each field activity are described.

III. Equipment / Materials

- Reagents: Distilled water in a squirt bottle and a standard potassium chloride solution
- Conductivity meter and electrodes
- Beakers or jars, plastic or glass
- Spare alkaline batteries, D-cell
- Reagent Preparation:
  - Stock potassium chloride (KCl) solution (1.00 N): Dissolve 74.555 g KCl in distilled water and dilute to 1,000 mL in a volumetric flask
  - Standard potassium chloride solution (0.01 N): Dilute 10.0 mL of stock 1.00 N KCl solution to 1,000 mL with distilled water using a volumetric pipet and flask

IV. Procedures / Guidelines

Groundwater

Detection limit = 1 µmho/cm at 25°C; range = 0.1 to 100,000 µmho/cm;
10 µmhos/cm = 1 mS/m

Calibration Check

Check instrument calibration before initial daily use, and at least once every 4 hours or every five samples, whichever is less. Check instrument with standard solution. Deviations should be noted in the field log book.

1. Turn on instrument.

2. Hit mode key until "°C" symbol is flashing to indicate temperature corrected results (conductivity units should be μmhos).
3. Read standard and note results.
4. Rinse probe with deionized water.
5. Run sample and record results.
6. Rinse with deionized water when done.

Decontaminate conductivity meter before use at each sample location. Rinse probe with distilled water before storage each day. Check meter for battery charge and physical damage each day. Store meter and conductivity standard in a cool, dry environment.

Operation Procedure

1. Perform calibration at the beginning and the end of the day.
2. Switch mode to "Temperature". Allow time for the probe temperature to come to equilibrium with that of the water before reading. Read the temperature on the bottom scale of the meter in degrees Celsius.
3. Switch mode to ×100. If the reading is below 50 on the 0 to 500 range (5.0 on the 0 to 50 mS/m range), switch to ×10. If the reading is still below 50 (5.0 mS/m), switch to the ×1 scale. Read the meter scale and multiply the reading by the mode factor. The answer is expressed in Fohms/cm. Measurements are not temperature compensated.
4. When measuring on the ×100 and ×10 scales, depress the "CELL TEST" button. The meter reading should fall less than 2 percent; if greater, the probe is fouled and the measurement is in error. Clean the probe and remeasure.

Operating Suggestions

- Obstructions near the probe can disturb readings.
- When the calibration test indicates low readings, the probable cause is dirty electrodes. Hard water deposits, oil, and organic matter are the most likely contaminants.
- Caution: Do not touch the electrodes inside the probe. The plating material is soft and can be scraped off.
- If cleaning does not restore the probe performance, replatinizing may be required. Always rinse the probe thoroughly in tap water, then in distilled or DI water after cleaning and before storage. Note that it is best to store conductivity cells in DI water. Collect rinsate water for storage pursuant to the Waste Management Plan.
- Most problems in obtaining good records with monitoring equipment are related to electrode fouling and inadequate sample circulation.
- Decontaminate conductivity meter before use at each sample location. Rinse probe with distilled water before storage each day. Check meter for battery charge and physical damage each day. Store meter and conductivity standard in a cool, dry environment.

- Water temperature readings can be taken using the conductivity meter. Switch from conductivity mode to temperature mode, and record the reading in the field notebook.

V. Attachments

- None.

VI. Key Checks / Items

- Document any deviations from above procedure.
- Check battery.
- Check calibration.
- Clean probe with deionized water when done.
- When reading results, note sensitivity settings.

VII. Preventive Maintenance

- Refer to operations manual for recommended maintenance.
- Check batteries. Have a replacement set on hand.

STANDARD OPERATING PROCEDURES

Field Measurements of Oxidative-Reductive Potential

I. Purpose

To provide a general guideline for the field measurement of oxidative-reductive potential (ORP) in water samples.

II. Scope

Standard field ORP determination techniques for use on surface water and groundwater samples.

III. Equipment / Materials

- 0.1 M potassium ferrocyanide
- 0.05 M potassium ferricyanide
- Hach cat. no. 50280-05 filling solution
- Demineralized water in a squirt bottle
- ORP meter
- 2, ×100ml volumetric flasks
- Beakers
- Glassware that has been washed with soap and water, rinsed twice with hot water, and then rinsed twice with demineralized water

IV. Procedures / Guidelines

Procedure

1. Before going into the field:
   a. Check batteries.
   b. Obtain fresh standard solutions.
2. Calibrate meter using following calibration procedure:
   a. Transfer 100 ml of 0.1 M potassium ferrocyanide to a 150 ml beaker. Place electrode in the solution and wait until the reading stabilizes. The potential should be about 234 mV.
   b. Rinse the electrode with demineralized water and repeat with 0.05 M potassium ferricyanide. The potential should read about 300 mV.
3. Pour sample into a clean beaker.

4. Rinse electrode with demineralized water between samples.
5. Immerse electrode in sample solution. Record ORP reading.
6. Recheck calibration with iron solutions after every 10 samples.

Decontaminate ORP meter before use at each sample location. When not in use, the electrode may be stored dry in an open-air environment. Remove salt crystals on the outside of the electrode sleeve by rinsing with demineralized water then drain the filling solution from the chamber. Flush the chamber with demineralized water and store dry. Check meter for battery charge and physical damage each day. Store meter and ORP calibration solution in a cool, dry environment.

General

1. The filling solution is Hach cat. no. 50280-05.
2. Following field measurements:
   a. Report any problems.
   b. Compare with previous data.
   c. Clean all dirt off of the meter and from inside the case.
   d. Store electrode in pH 4 buffer solution.
3. Accuracy and precision are dependent on the instrument used. Refer to the manufacturer's manual. Expected accuracy and precision are ± 10 mV.

IV. Attachments

- None.

V. Key Checks / Items

- Check batteries.
- Calibrate.

VI. Preventive Maintenance

- Refer to the operation manual for recommended maintenance.
- Check batteries. Have a replacement set on hand.

STANDARD OPERATING PROCEDURES

Volatile Organic Vapor Monitoring with the OVA Instrument

I. Purpose

To provide general guidelines for the calibration and use of an organic vapor analyzer (OVA) flame ionization detector.

II. Scope

This is a broad guideline for the use of an OVA. For specific instructions, refer to the manufacturer's instructions and the operations and maintenance manual.

III. Equipment / Materials

- Instruction Manual
- OVA organic vapor analyzer
- Calibration span gas (100 ppm methane in air)
- Regulator for span gas cylinder
- For continued use, a source of 99.999-percent pure hydrogen for recharging the internal tank

IV. Procedures / Guidelines

Only properly trained personnel should used this instrument. For specific instructions, see manufacturer's instruction manual.

Start Up

1. Attach meter/probe assembly.
2. Turn pump switch on and check battery by moving "INSTR" switch to "BATT" position.
3. Turn "INSTR" switch on and wait 5 minutes.
4. Zero instrument with "Calibrate" knob.
5. Open hydrogen gas valve.
6. Depress igniter button until burner flame ignites.
7. Use "Calibrate" knob to zero out ambient background.

8. Calibrate unit to 100ppm with methane span gas, adjusting the "Gas Select" (span control) pot. Note the source of methane standard, date acquired, and by whom.
9. Unit is ready to use. Do not immerse probe in solid or liquid samples. Record readings in ppm as indicated on the meter.

Shut Down

1. Close hydrogen valve.
2. Move "INSTR" and pump switches to off.
3. Charge unit (it will take about 1 hour of charging for each hour of operation).

Caution

Hydrogen is very explosive. Only trained personnel shall fill hydrogen tanks.

V. Key Checks / Items

- Open hydrogen gas valve.
- Light flame.
- Close hydrogen gas valve when done.
- Recharge battery.

VI. Preventive Maintenance

A complete preventative maintenance program is beyond the scope of this SOP. For specific maintenance instructions, refer to the manufacturer's operations manual.

- Keep spare OVA available whenever field use of the instrument is required.
- Use only 99.999-percent pure hydrogen.
- Keep spare supply of valve seals on hand so that hydrogen leaks can be repaired without returning the unit.
- Charge batteries daily.
- Allow batteries occasionally to discharge completely before recharging to prevent battery "memory" from occurring.

STANDARD OPERATING PROCEDURES

Field Filtering of Aqueous Samples

I. Purpose

To provide a general guideline for the field filtering of water samples for dissolved metals analysis.

II. Scope

Standard method of field filtering techniques.

III. Equipment / Materials

- Pre-preserved sample container with HNO_3
- DI water
- Peristaltic Pump
- 0.45 micron cellulose acetate filter
- Disposable Teflon tubing

IV. Procedures / Guidelines

Procedure

1. Place approximately 1.5 feet of disposable Teflon tubing into the peristaltic pump, or remove the peristaltic pump tubing and replace with new.
2. With the peristaltic pump running, purge the inlet and outer tubing with distilled water. Make sure all of the distilled water is out of the tubing before filtering the sample.
3. Submerge the inlet tube from the peristaltic pump into the sample to be filtered.
4. Attach a new in-line filter to the outlet tube of the peristaltic pump, making sure that the sample flow is in the same direction as the arrow on the filter housing.
5. Turn on the peristaltic pump and discard a small amount of the initial sample that flows out of the filter. Pump the remainder of the filtered sample into a clean bottle.
6. Add the required preservative to the filtered sample.
7. Discard the filter.
8. Repeat steps.

V. Attachments

None.

VI. Key Checks / Items

- All purge water must be distilled or deionized.
- Preserve samples when done.

STANDARD OPERATING PROCEDURES

Field Measurement of Dissolved Oxygen

I. Purpose

The purpose of this technical practice is to provide a general guideline for the field measurement of dissolved oxygen in water samples.

II. Scope and Applicability

This technical practice provides information on the equipment, materials, and procedures used for standard field dissolved oxygen determination in water samples.

III. Equipment / Materials

- Dissolved oxygen meter
- Dissolved oxygen probe
- Potassium chloride (KCl) probe refill solution
- Spare probe membranes
- Spray bottle with deionized water

IV. Procedures / Guidelines

Procedure

1. Before going into the field:
   a. Check batteries.
   b. Perform calibration.
   c. Check probe membrane.
2. Record instrument make, model, and serial number in the log book or data form.
3. Calibrate meter using the calibration procedure per the manufacturer's recommendation and a duplicate reading every 10 samples.
4. Pour the collected water sample into a clean beaker.
5. Rinse probe with deionized water.
6. Immerse the probe in the sample. Record the dissolved oxygen reading in the log book or data form, and record the results once the readings have stabilized.
7. Decontaminate the probe and the beaker and then cover to protect them from contamination.

General

1. Measurement of dissolved oxygen is temperature dependent. Therefore, temperature correction must be accurate when calibrating.

2. Following field measurements:

   a. Record any problems.
   b. Compare with previous data and note any large variances.
   c. Clean all dirt off of the meter and from inside the case.
   d. Store probe in calibration container with wet towel/sponge.

3. Accuracy and precision are dependent on the instrument used. Refer to the manufacturer's manual. Expected accuracy and precision are ± 0.1 mg/L.

V. Key Checks / Items

- Check batteries.
- Check the membrane.
- Calibrate.
- Decontaminate and cover the probe.

STANDARD OPERATING PROCEDURES

Water Level Measurements

I. Purpose

A general guideline for the measurement of water levels in monitoring wells and piezometers.

II. Scope

Standard method of water level measurements.

III. Equipment / Materials

- Water level indicator
- Deionized water
- Squirt bottles
- Paper towels

IV. Procedures / Guidelines for Water Level Measurements

1. Uncap the well and immediately place the photoionization meter at the wellhead for readings.
2. Vent well caps and allow water levels to reach static levels for at least 15 minutes.
3. Decontaminate water level indicator with deionized water.
4. Test battery on water level indicator.
5. Measure depth to water by:
    a. Adjusting gain/sensitivity (while probe is dry) to the maximum sensitivity that does not activate the audible sensor.
    b. Lower probe into the well slowly until the audible sensor activates.
    c. Raise and lower the probe slowly to precisely measure the top of the water.
    d. Hold the tape (indicating depth) against the north top edge of the well casing (the designated measuring point) and read depth to water to the nearest 0.01 feet.
6. Record depth to water.
7. Measure total well depth by:
    a. Turn gain/sensitivity off.

b. Lower probe into the well until the probe contacts the bottom.

c. Raise and lower the probe slowly so that the probed is vertical and not leaning across the diameter of the well.

d. Hold the tape (indicating depth) against the north top edge of the well casing and read depth to the nearest 0.01 feet.

V. Key Checks / Items

- Vent wells before measurement.
- Use the same location on the well casing to ensure comparability of readings.
- Decontaminate water level indicator with deionized water.

Well Purging

I. Purpose

The purpose of this procedure is to provide general reference information on well purging by both the bailing method and the pumping method prior to the sampling of groundwater wells. The methods and equipment described are for the purging of water samples from the saturated zone of the subsurface.

II. Scope

Methods for purging from completed wells include the use of pumps, bailers, and various types of samplers. The primary considerations in obtaining a representative sample of groundwater are to avoid collection of stagnant (standing) water in the well and to avoid physical and chemical alteration of the water due to purging and sampling techniques. In a non-pumping well, there will be little or no vertical mixing of water in the well pipe or casing, and stratification will occur. The well water in the screened section will mix with the groundwater due to normal flow patterns, but the well water above the screened section can remain isolated and become stagnant.

III. Equipment / Materials

- Bailers
- Polypropylene bailer line (or approved equal)
- Retractable engineer's measuring tape (Calibrated to 0.01 foot)
- Water level indicators
- Swabbing equipment
- pH & turbidity meter
- Specific conductance/temperature meter
- Drums to contain the development water
- Groundwater sampling form
- Field logbook
- Calculator
- Plastic sheeting
- Gasoline or electric purge pump
- Power source

IV. Procedures / Guidelines

General

Before groundwater sampling begins, wells will be purged of stagnant water.

Wells screened in low permeability formations (i.e., wells that can be purged dry) will be purged as follows:

1. Pump or bail the well dry.
2. Measure the field parameters for every well volume purged. The measurements indicate stable groundwater conditions when there is less than a 10 percent variability of parameters among three well volumes.
3. Wait a minimum of 15 minutes, allowing the well to recover after purging. When the well recovers to 80 percent of its original level or when a sufficient volume of water exists for the intended analysis, the sampling may begin.

Wells screened in permeable formations will be purged as follows:

1. Remove 5 well volumes (calculate this volume using the equation shown below).

   $$V = (\pi \times r^2)\, H \times 5 \text{ well volumes} \times 7.48$$

   where,

   V = total volume of water needed to purge in gallons
   r = inside radius of well in feet
   H = height of water column in well feet (depth to bottom of well minus depth to water)

2. Collect field parameters after five well volumes have been purged.
3. Limit the amount of air and turbulence into the formation during purging to prevent potential alteration of the samples.

Specific Procedures

- Work crew members must use either new disposable gloves or decontaminated reusable gloves.
- To prevent cross contamination of wells, upgradient and background wells should be purged and sampled first.
- Measure background organic vapors in the air using photoionization/flame ionization meter. Open the well casing cover, remove the well cap, and sample the well head space (air inside the well) for gaseous contaminants using the photoionization/flame ionization meter. If the organic vapor concentrations is equal to or greater than 1000 ppm, immediately recap the well and inform the Field Team Leader.
- Measure the "depth of water" in the well in accordance with the water level measurement SOP, *Water Level Measurements*.
- Calculate the volume of water in the well, record this data in the field notebook, and calculate the volume of water required to be purged. Normally, the well will be purged of three to five volumes of water until the temperature, pH, and conductivity have stabilized.

Procedure for Well Purging by Bailing

- Remove protective foil from bailer.
- To prevent the bailer from getting stuck in the well, the loose end of the rope should be cut short enough not to extend beyond the sloping portion of the bailer barrel.
- The bailer will be slowly lowered into the well to the desired level.
  Note: If resistance is encountered during the lowering of the bailer into the well, THE BAILER SHOULD BE WITHDRAWN FROM THE WELL IMMEDIATELY, and the Field Team Leader informed.
- The rope will be secured to the protective casing of the well or to the sampling person's wrist.
- The bailer will be withdrawn from the well and the purged water poured into the receptor drum or bulk container.
- The bailer will be lowered, and a full bailer will be repeatedly withdrawn until the required minimum of three to five well volumes have been purged.
- Record the total volume of groundwater removed on the Groundwater Sampling Form and in the field logbook.
- Purging will continue until the physical parameters have stabilized so that pH is 0.1 su, conductivity is 10 µmhos, temperature is 0.5°C, and turbidity is less than 10 NTU within three successive intervals, each separated by five minutes, or until a maximum of 10 well volumes are removed.
- Whenever the receptor drums have been filled, the water shall be stored, analyzed, and disposed of in accordance with the project-specific Work Plan.
- Decontaminate the bailers per SOP *Field Sampling Equipment Decontamination.*

Procedure for Well Purging by Pumping

- Remove the protective foil from the purge pump.
- Lower the purge pump into the well until it is submerged.
  Note: If resistance is encountered during the lowering of the pump into the well, THE PUMP SHOULD BE WITHDRAWN FROM THE WELL IMMEDIATELY, and the Field Team Leader informed.
- Direct the pump discharge hose into the receptor drum and start pumping in accordance with the pump's operation manual.
- Record the total volume of groundwater removed from the well on the Groundwater Sampling Form and in the field logbook. Collect a minimum of three samples during purging, and note the clarity of the sample, pH, conductivity, and temperature measurements of the sample in the purge notebook.
- Purging will continue until the physical parameters have stabilized so that pH is 0.1 su, conductivity is 10 µmhos, and temperature is 0.5°C, and turbidity is less than 10 NTU

within three successive intervals, each separated by five minutes, or until a maximum of 10 well volumes are removed.

- Whenever the receptor drums have been filled, the water shall be stored, analyzed, and disposed of in accordance with the project-specific Work Plan.
- Carefully withdraw the purge pump from the well.
- Decontaminate the pump and hose per SOP *Field Sampling and Equipment Decontamination*.

V. Attachments

None.

VI. Key Checks / Items

None.

STANDARD OPERATING PROCEDURES

Soil Sampling Procedures

I. Types of Soil Samples

An individual sample collected from a single location at a specific time, or period of time, not exceeding 15 minutes is a grab sample. Grab samples are associated with surface water, groundwater, wastewater, waste, contaminated surfaces, soil, and sediment sampling. A sample collected from individual grab samples is collected on an areal or cross-sectional basis. Composites shall be made up of equal volumes of grab samples. Each grab sample shall be collected in an identical manner.

II. Hand-Troweling

Those methods are used primarily to collect surface and shallow subsurface soil samples. Surface soils are generally classified as soils between the ground surface and 6 to 12 inches bgs. The shallow subsurface interval may be considered to extend from about 12 inches bgs to a site-specific depth at which sample collection using manual or hand-powered methods becomes impractical.

Surface soils may be collected using a wide variety of equipment. Spoons, shovels, hand augers, push tubes, and posthole diggers made of the appropriate material may be used to collect surface soil samples.

Surface samples are removed from the ground and placed in pans, where they may be mixed thoroughly before sample containers are filled. If a thick, matted root zone is encountered at the surface, it should be removed before the sample is collected.

It is extremely important that soil samples be mixed as thoroughly as possible to ensure that the sample is representative of the interval sampled. After collection, all sample handling should be minimized. Personnel should use extreme care to prevent sample contamination. If samples are placed in an ice chest, personnel should be sure that melted ice can not cause sample containers to become submerged, as this may result in sample cross-contamination. Plastic bags, such as Zip-Lock® bags, should be used when small sample containers, such as VOA or bacterial samples, are placed in ice chests to prevent cross-contamination.

III. Backhoes

Backhoes will be used during test pitting activities. Samples will be collected directly from the backhoe bucket using a stainless steel spoon. Samples must be collected from material which has not been in contact with the bucket surface.

Any time a vertical or near-vertical surface, such as is achieved when shovels or backhoes are used for subsurface sampling, is sampled, the surface should be dressed to remove smeared soil. This is necessary to minimize the effects of cross-contamination due to the smearing of material from other levels.

IV. Collection of Soil Samples for Volatile Organic Analyses

Samples should be collected in a manner that minimizes disturbance of the sample. For example, when sampling with a hand-held auger, the analysis sample may be collected directly from the auger bucket or immediately after an auger bucket is emptied into the bowl. The sample should be placed in the appropriate container with no head-space, if possible, as is the practice with water samples. Samples for VOA are not mixed.

V. Sample Mixing

It is extremely important that soil samples from non-VOC analyses be mixed as thoroughly as possible to ensure that the sample is representative of the interval sampled. After collection, all sample handling should be minimized. Personnel should use extreme care to ensure that samples are not contaminated. If samples are placed in an ice chest, personnel should ensure that melted ice cannot cause sample containers to become submerged, as this may result in sample cross-contamination. Plastic bags, such as Zip-Lock® bags, should be used when small sample containers (e.g., VOA samples) are placed in ice chests to prevent cross-contamination.

Once a sample has been collected, it may have to be split into separate containers for different analyses. A true split of soil, sediment, or sludge samples is almost impossible to accomplish under field conditions. The higher the moisture content, the more difficult it is to split the sample. It is extremely important that soil samples be mixed as thoroughly as possible to ensure that the sample is as representative as possible of the sample interval. The most common method of mixing is referred to as quartering. The soil in the sample pan is divided into quarters. Each quarter is mixed, then all of the quarters are mixed into the center of the pan. This procedure is followed several times until the sample is adequately mixed. If round bowls are used for sample mixing, adequate mixing is achieved by stirring the material in a circular fashion and occasionally turning the material over. Soil and sediment samples collected for purgeable organic compound analyses should not be mixed. The 2-ounce (60-mL) sample container should be filled completely; no head space should remain in the sample containers.

VI. Special Precautions for Trace Contaminant Soil Sampling

All soil sampling equipment used for sampling for trace contaminants should be constructed of stainless steel where possible. Pans used for mixing shall be made of stainless steel, Pyrex®, or equivalent glass. In no case will chromium, cadmium, or galvanized plated or coated equipment be used for soil sampling operations. Similarly, no painted or plastic equipment shall be used. All paint and primer must be removed from soil sampling equipment by sandblasting or other means before such equipment can be used for collecting soil samples.

Some contaminants can be detected in the parts per billion and parts per trillion range. Extreme care must be taken to prevent cross-contamination of the samples. The following precautions shall be taken when trace contaminants are of concern:

- A pair of new, clean, disposable gloves will be worn each time a different location is sampled. Gloves should be donned immediately prior to sampling.
- Sample containers for source samples or samples suspected of containing high concentrations of contaminants shall be placed in separate plastic bags immediately after collecting, preserving, tagging, etc.
- Samples of waste or highly contaminated samples shall never be placed in the same ice chest as environmental samples. It is good practice to enclose waste or highly contaminated samples in a plastic bag before placing them in ice chests. Ice chests or shipping containers for source samples, or samples suspected to contain high concentrations of contaminants, shall be lined with new, clean, plastic bags.
- When sampling surface waters, the water sample should always be collected before the sediment sample is collected.
- Sample collection activities should proceed progressively from the suspected least-contaminated area to the suspected most-contaminated area.
- Personnel should use equipment constructed of Teflon, stainless steel, or glass that has been properly precleaned (Appendix B) for collecting samples for trace metals or organic compounds analyses. Teflon or glass is preferred for collecting samples where trace metals are of concern. Equipment constructed of plastic or PVC shall **not** be used to collect samples for trace organic compounds analyses.

STANDARD OPERATING PROCEDURES

Soil Vapor Parameter Measurement

I. Purpose

The purpose of this procedure is to monitor the oxygen, carbon dioxide, methane, lower explosion limit (LEL), and total organic hydrocarbon concentrations present in soil vapor.

II. Scope

Standard field procedure for measuring the oxygen, carbon dioxide, methane, lower explosion limit, and total organic hydrocarbon concentrations in soil vapor.

III. Requirements

Measuring points are shallow (vadose zone only) and intermediate depth (deep vadose zone within the LNAPL) piezometers.

IV. Equipment / Materials

- Landtec GA-90 gas analyzer (oxygen, carbon dioxide, LEL, and methane), and a MultiRAE organic vapor analyzer with photoionization detector (PID)
- 1 scfm vapor sampling vacuum pump
- Tygon and Teflon tubing, tubing connections
- 2-inch slip sleeve with gasket and labcock connections for measuring wells normally used for groundwater level measurements and/or sampling

V. Procedures / Guidelines

Procedure

1. Calibrate equipment according to manufacturer's instructions.
2. Connect magnehelic gauge with Tygon tubing to the labcock valve on the top of the piezometer. If well, connect gauge to the labcock connection to the slip sleeve. Record pressure indication on gauge.
3. Open labcock valve.
4. Connect air sampling pump to well or piezometer and purge for 5 minutes.
5. While air sampling pump is running, use Landtec GA-90 gas analyzer to measure oxygen, carbon dioxide, methane, and LEL.

6. While air sampling pump is running, use organic vapor analyzer to measure total vapor hydrocarbons.
7. Repeat steps at other locations.
8. Record readings.

VI. Attachments

None.

VII. Key Checks / Items

- Calibrate equipment prior to sampling.

STANDARD OPERATING PROCEDURES

Soil Gas Pressure Measurement

I. Purpose

The purpose of this procedure is to measure soil gas pressure at piezometers.

II. Scope

Standard field procedure for measuring soil gas pressures in piezometers.

III. Requirements

Soil gas pressure can be measured either in piezometers screened in the vadose zone or in monitoring wells open to the vadose zone. The screen depth of the well being used for measurement should be known beforehand. In addition, care should be exercised in making sure that an airtight seal between the gauge and the well exists.

IV. Equipment / Materials

- 0-to 1-inch water Dwyer megnehelic gauge
- Miscellaneous Tygon and Teflon tubing, tubing connections
- 2-inch slip sleeve with gasket and labcock connections for measuring wells normally used for groundwater level measurements and/or sampling

V. Procedures / Guidelines

Procedure

1. Connect megnehelic gauge with Tygon tubing to the labcock valve on the top of the piezometer. If measuring pressure at a monitoring well, connect the gauge to the labcock connected to the slip sleeve.
2. Open labcock valve and measure the soil pressure reading on the gauge.
3. Close the labcock valve and disconnect the tubing from the labcock.
4. Record pressure measurement.
5. Plot readings on figure that shows monitoring point locations.

VI. Attachments

None.

VII. Key Checks/Items

- Calibrate equipment prior to sampling.

STANDARD OPERATING PROCEDURES

Field Sampling Equipment Decontamination

I. Purpose

To provide general guidelines for the decontamination of soil sampling equipment, monitoring equipment, and sample containers used in potentially contaminated environments.

II. Scope

This is a general description of decontamination procedures. For specific deviations, see the unit-specific field sampling plans.

III. Equipment / Materials

- Demonstrated analyte-free deionized water
- Distilled water
- Alconox (or other phosphate free detergent) and water solution
- Isopropanol- DO NOT USE ACETONE
- Large plastic pails or tubs for detergent and water, scrub brushes, squirt bottles for detergent, methanol and water, plastic bags, and sheets
- U. S. Department of Transportation (DOT)-approved 55-gallon drum for disposal of waste

IV. Procedures / Guidelines

Sampling Equipment Decontamination

All soil, surface water, and sediment sampling equipment not associated with the drill rig and drilling will be decontaminated by personnel wearing disposable latex gloves or vinyl gloves using the following procedure:

1. Before entering the potentially contaminated zone, wrap soil contact points in clean plastic.
2. Wash all of the equipment surfaces that have contacted the potentially contaminated soil or water with TSP solution, using a brush as needed to remove particulate matter and surface films.
3. Rinse with potable tap water.

4. Rinse twice with methanol solution and air dry. DO NOT USE ACETONE.
5. Rinse with distilled water and air dry.
6. Wrap the equipment with aluminum foil, if appropriate, to prevent contamination if the equipment is to be stored or transported.
7. Collect all rinsate and dispose of it in a DOT-approved 55-gallon drum.

Monitoring Equipment Decontamination

1. Wrap soil contact points in plastic to reduce the need for subsequent cleaning.
2. Wipe all surfaces that have had possible contact with contaminated materials with a paper towel that has been wet with detergent solution; wipe with a towel wet with methanol solution; and wipe three times with a towel that has been wet with distilled water.
3. Dispose of all used paper towels in a DOT-approved 55-gallon drum.

Sample Container Decontamination

The outer surface of sample containers that have been filled in the field must be decontaminated before being packed for shipment or handled by personnel without dermal hand protection.

1. Then wipe container with a paper towel dampened with potable water.
2. Dispose of all used paper towels in a DOT-approved 55-gallon drum.
3. After the containers have been sealed, wipe the sample container with a paper towel dampened with detergent solution.

V. Key Checks / Items

- Clean with solutions of detergent, methanol (or isopropanol), and distilled water.
- Do not use acetone for decontamination.
- Drum all contaminated rinsate and materials.
- Decontaminate sample bottles before relinquishing them to anyone.
- Document any deviations from above procedure.

STANDARD OPERATING PROCEDURES

Groundwater Sampling

I. Purpose

The purpose of this standard operating procedure is to obtain groundwater samples that are representative of the source from which they are taken, and to minimize sampler exposure to groundwater contaminants. This document covers groundwater sampling both from monitoring wells and from temporary well points.

II. Scope

This procedure provides information on the proper equipment and techniques to be used in groundwater sampling. This information will facilitate planning of the field sampling effort by describing standard sampling techniques.

III. Equipment / Materials

Ideally, sample withdrawal equipment should be completely inert, economical, easily decontaminated, easily sterilized, reusable, able to operate at remote sites in the absence of power sources, and capable of delivering variable rates for well purging and sample collection.

The following pieces of equipment may be needed to collect groundwater samples:

- pH meter/paper
- Dissolved oxygen meter
- Specific-conductivity/temperature meter
- Wide-mouth jar for parameter measurements
- Appropriate keys (for locked wells)
- Tape measure
- Pipe wrenches
- Water level indicator
- Oil-water interface probe
- Flow meter
- Pumps: centrifugal, positive displacement, or peristaltic pumps where applicable, or submersible pumps and electrical power generating units or bladder pumps with compressed air sources, where applicable

- Sample tubing such as Teflon, polyethylene, and polypropylene. The tubing type shall be selected based on specific site requirements, and it must be chemically inert to the groundwater being sampled
- Teflon bailers
- Teflon coated wire, stainless steel single strand wire, polypropylene monofilament line, or 1/4-inch nylon rope and tripod-pulley assemble (if necessary)
- Pails (plastic, graduated)
- Large container for purged groundwater
- Plastic sheeting
- Sample containers
- Coolers for sample shipping and cooling
- Camera and film
- Sample table and plastic cover
- Plastic trash bags
- Indelible marking pens
- Black permanent ink pen (Sharpie™ brand or similar)
- Field sampling log books and form
- Duct tape
- 0.45-micron filter and in-line sampling equipment

IV. Procedures / Guidelines

Temporary wells points may be sampled immediately after installation, since there is not any non-representative formation water to be purged.

Monitoring wells require purging. Generally, wells should be sampled within 3 hours of purging. However, wells with poor recharge should be sampled within 24 hours of purging. "Poor recharge wells" are those that cannot recharge to 80 percent of the original volume within 8 hours. Sampling of wells that do not recharge adequately for sampling within 24 hours will be determined on a case by case basis.

All sampling equipment must be decontaminated in accordance with the SOP *Field Sampling Equipment Decontamination* before the start of sampling.

Well sampling shall be taken in order from wells with the lowest historic concentrations of Chemicals of Interest (COIs) to the highest. This will reduce the risk of cross contamination between wells.

V. Sampling Procedure

Groundwater is to be sampled using the following steps:

1. *Take Groundwater Parameter Measurements*: Temperature, pH, conductivity, and eH parameters representative of the sample that is collected should be recorded prior to sample collection.

2. *Take VOA Sample First:* Efficiency and care must be utilized to obtain representative samples for volatile organic analysis. Unnecessary delays or poor sampling techniques will lead to loss of the volatile constituents from the sample. Prevent unnecessary stripping of volatile constituents from the sample by minimizing turbulence and aeration when filling the sampling device and when filling the sample container. Quickly fill the sample container until a positive meniscus is achieved above the rim of the container, and cap the container immediately. Gently tap the sample container to dislodge any air bubbles and verify that no bubbles are present. If bubbles are detected, immediately uncap the sample, add additional sample from the bailer until a positive meniscus is re-established, and immediately recap the sample and check the sample for bubbles. Repeat this step until the volatile organics sample contains no bubbles and all required samples are obtained.

3. *Sample Other Constituents*: To ensure that groundwater samples are representative of actual conditions, samplers must work efficiently to minimize the loss of groundwater contaminants and the introduction of foreign contaminants. To prevent the contamination of samples, the sample bottles should be opened only when receiving sample preservatives or groundwater samples, and closed immediately afterwards. To prevent the introduction of foreign contaminants into the well, sample bottles should be held away from the well opening when receiving samples, and the purging and sampling equipment, such as or pump tubing and bailing rope, should not be allowed to touch the ground or other potentially contaminating objects.

   The sampler should quickly add the sample into the sample containers while minimizing aeration and loss of the volatile contaminants. Samples collected for analysis of volatile constituents will be collected first, followed by samples collected for analysis of total organic carbon (TOC), total organic halogens (TOX), and those constituents which require field filtration or field determination after the collection of volatile organics. Large volume samples for extractable organic compounds, total metals, etc., should be collected last.

   When a sample bottle is filled, the bottle must be tightly capped as soon as possible. This section represents general instructions, not a specific step.

5. *Filter Dissolved Metals Sample:* Groundwater samples collected for dissolved metals analysis will be field filtered using an in-line disposable filter method. Groundwater samples will be filtered by inserting a filter directly into the sample tubing, or immediately after collection through the use of a pressure filtration system that uses nitrogen gas to "push" the sample through the filter media (OEPA, 1995). A new, disposable 0.45-micron filter will be used for each sample; if groundwater is highly turbid, more than one filter may be used. Any non-disposable field filtering equipment

will be decontaminated before and after filtering according to the procedures listed in the SOP. Immediately after filtering, samples will be containerized in bottles containing nitric acid for acidification to a pH of less than 2.

6. *Secure the Well*: After sampling, replace the well cap and lock the well.
7. *Prepare Samples*: As soon as all samples are collected, promptly prepare the samples for shipment in accordance with the SOP *Sample Handling and Custody Requirements*. Immediately place all samples on ice in a cooler when in the field.
8. *Document Sampling*: Record all sampling information in the Field Sampling Log Book or Sample Form.
9. *Decontaminate Equipment:* Decontaminate all equipment as specified in the Field Sampling Equipment Decontamination SOP.

Collection of Split Samples or Field Duplicates

When field duplicates are required, these samples will be collected concurrently. For instance, containers for all volatile organic analyses will be filled first and together, all semi-volatiles together and in proper sequence, and so forth until all sample parameters are in the proper containers.

Record all sample identifiers used for duplicates or splits by other organizations in the field book or field form. Note any deviations by the other organization from the project SOPs.

Sample Containers

For most samples and analytical parameters, either glass or plastic containers are satisfactory. The QAPP describes the required sampling containers for various analytes at various concentrations.

Preservation of Samples and Sample Volume Requirements

Sample preservation techniques and volume requirements are specified in the QAPP, and are constituent and matrix-specific. Sample containers will be pre-preserved at the laboratory. The field teams should take proper care when handling these containers. Should the preservative become diluted or be spilled, notify the FTL and acquire new bottles to ensure the samples are properly preserved.

VI. Attachments

Groundwater Sampling Form.

Appendix D

Chain-of-Custody and Sample Tag

USEPA Contract Laboratory Program
Generic Traffic Report / Chain-of-Custody Record

Case No.

DAS No. [redacted]

Region:	05
Project Code:	[redacted]
Account Code:	
CERCLIS ID:	[redacted]
Spill ID:	[redacted]
Site Name/State:	[redacted]
Project Leader:	[redacted]
Action:	[redacted]
Sampling Co.:	CH2MHill

Date Shipped:	[redacted]
Carrier Name:	[redacted]
Airbill:	[redacted]
Shipped to:	[redacted]

Sampler (Signature)

[redacted]

Relinquished By:	Date / Time	Received By:
[redacted]	[redacted]	
Relinquished By:	**Date / Time**	**Received By:**
Relinquished By:	**Date / Time**	**Received By:**

SAMPLE No.	MATRIX/ SAMPLER	CONC/ TYPE	ANALYSIS/ TURNAROUND	TAG No./ Preservative	STATION LOCATION	SAMPLE COLLECT DATE/TIME	SAMPLE No.	QC TYPE
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]		--
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]		--

Shipment for Case Complete? N	Sample(s) to be used for Laboratory QC:	Additional Sampler Signature(s):	Chain of Custody Seal Number
			[redacted]

Analysis Key: Concentration: L = Low M = Low/Medium H = High Type/Designate: Composite = C Grab = G

PCP=PENTACHLORPHENOL

PR:provides preliminary results. Requests for preliminary results will increase analytical costs.

Send Copy to: Contract Laboratory Analytical Services Support, 2000 Edmund Halley Dr, Reston, VA. 20191-3436 Phone: 703/264-9348 Fax 703/264-9222

TR Number: 05-405012729-040301-0001

F2V4.0

Case # or Project Code	Sample Number	Month/Day/Year	Time	DESIGNATE Comp.	DESIGNATE Grab	Station Number and Location	Samplers (signatures)

PRESERVATIVE: H_2SO_4 ☐ IGE ☐
HCL ☐ HNO_3 ☐ NaOH ☐ Other ☐

ANALYSES

VOA		METALS	
ABN		CYANIDE	
PEST/PCB			
		Mercury	
Pesticides		Fluoride	
Herbicides		Nitrate/Nitrite	
PCB		TOC	
PCDD/PCDF		BOD	
2,3,7,8-TCDD		COD	
Ames Mutagen		TDS	
Asbestos		TSS	
Phosphorus		O&G	
Phenols		Sulfate	
PAH		Chloride	
TCLP		Sulfide	
TOX		Ammonia	
CBOD		Alkalinity	
Bio-Acute		Acidity	
Bio-Chronic		TKN	

Matrix:

Remarks:

USE FOR MS/MSD ☐

Tag Number	Lab Sample Number
5-036666	