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MULTI-AREA QUALITY ASSURANCE PROJECT PLAN

12th Street Landfill Site (Operable Unit No. 4) and Plainwell Mill Site (Operable Unit No. 7)

Allied Paper, Inc./Portage Creek/
Kalamazoo River Superfund Site
Allegan County, Michigan

Revision 03, Addendum 04
June 26, 2009

Submitted in connection with Phase II Remedial Investigation Work Plan, Plainwell Mill and the Remedial Action Work Plan, 12th Street Landfill

Prepared by Conestoga-Rovers & Associates
on behalf of Weyerhaeuser Company

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LIST OF ACRONYMS AND ABBREVIATIONS

µg/L	micrograms per liter
µg/kg	micrograms per kilogram
AA	atomic absorption
ARAR	Applicable, or Relevant and Appropriate Requirement
ASTM	American Society for Testing and Materials
BFB	p-bromofluorobenzene
BNA	base-neutral-acid extractable
CAS	Columbia Analytical Services
CCB	continuing calibration blank
CCC	calibration check compound
CCV	continuing calibration verification
CD	Consent Decree
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
COC	Chain-of-Custody
COPC	constituent of potential concern
CRA	Conestoga-Rovers & Associates
CVAA	cold vapor atomic absorption
DFTPP	decafluorotriphenylphosphine
DI	deionized
DO	dissolved oxygen
DQI	data quality indicators
DQO	Data Quality Objective
ECD	electron capture detector
EDD	electronic data deliverable
Eh	redox
FB	field blank
FS	Feasibility Study
FSP	Field Sampling Plan
GC/MS	gas chromatograph/mass spectrophotometer
GRCC	Generic Residential Cleanup Criteria
HSP	Health and Safety Plan
ICB	initial calibration blank
ICP	inductively coupled plasma
ICPMS	inductively coupled plasma mass spectroscopy

LIST OF ACRONYMS AND ABBREVIATIONS
(Continued)

ICS	interface check samples
ICV	initial calibration verification
IDW	investigation-derived waste
kg	kilogram
KRSG	Kalamazoo River Study Group
L	liter
LCS	laboratory control sample
LCSD	laboratory control sample duplicate
LRA	linear range analysis
MDEQ	Michigan Department of Environmental Quality
MDL	Method Detection Limit
MS	matrix spike
MS/MSD	matrix spike/matrix spike duplicate
MSD	matrix spike duplicate
NCP	National Contingency Plan
NIST	National Institute of Standards and Technology
NTU	nephelometric turbidity unit
OSC	On-Scene Coordinator
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
pH	negative logarithm (base 10) of hydrogen ion activity
PID	photoionization detector
PQO	Project Quality Objective
POTW	publicly-owned treatment works
PM	Project Manager
QA	quality assurance
QA/QC	quality assurance/quality control
QAPP	Quality Assurance Project Plan
QC	quality control
QL	Quantitation Limit
RASs	routine analytical service
RCRA	Resource Conservation and Recovery Act
RD/RA	Remedial Design/Remedial Action

LIST OF ACRONYMS AND ABBREVIATIONS
(Continued)

RF	response factor
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
ROD	Record of Decision
RPD	relative percent difference
RL	reporting limit
RPM	Remedial Project Manager
RSD	relative standard deviation
RT	retention time
SAP	Sampling and Analysis Plan
SAS	special analytical services
SOP	standard operating procedure
SOW	Statement of Work
SPCC	system performance check compound
SRI/FS	Supplemental Remedial Investigation/Feasibility Study
SRM	standard reference material
SW846	Test Methods for Evaluating Solid Waste, 1996
TAL	Target Analyte List
TCL	Target Compound List
TCLP	Toxicity Characteristic Leaching Procedure
TCRA	Time-Critical Removal Action
TEMP	temperature
TB	trip blank
TSS	Total suspended solids
U.S. EPA	United States Environmental Protection Agency
UFP	Uniform Federal Policy
VOC	volatile organic compound
WATS	Weyerhaeuser Analytical Testing Services

1.0 INTRODUCTION

On February 22, 2005, Weyerhaeuser Company (Weyerhaeuser) entered into a Consent Decree (CD) with the United States Environmental Protection Agency (U.S. EPA) for the Design and Implementation of Certain Response Activities at the 12th Street Landfill site (Operable Unit No. 4) and the Plainwell Mill site (Operable Unit No. 7). Both sites are part of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund site (Figure 1-1), which is located in southwestern Michigan. A Statement of Work (SOW) for the Remedial Design/Remedial Action (RD/RA) at the 12th Street Landfill site was attached to the CD. A SOW for the Remedial Investigation/Feasibility Study (RI/FS) at the Plainwell Mill site was subsequently issued by the U.S. EPA, with an effective date of August 17, 2006.

In late February 2007, the U.S. EPA authorized a Time-Critical Removal Action (TCRA) to remove polychlorinated biphenyl (PCB)–contaminated sediment in the former Plainwell Impoundment (a section of Operable Unit #5 of the Allied Paper/Portage Creek/Kalamazoo River Superfund Site). This work was authorized through an administrative settlement agreement and Order on Consent for Removal Action (V-W-07-C-8-63). As part of the TCRA, the earthen section of the Plainwell Dam was removed and the Kalamazoo River was rerouted through the former powerhouse discharge channel. The 12th Street Landfill abuts the river and is located directly downstream of the earthen section of the Plainwell Dam on the western side of the former powerhouse discharge channel. The Plainwell Mill also abuts the Kalamazoo River and PCB-containing materials have been documented along the riverbank at the Mill. The change in the Kalamazoo River channel will result in an increased river gradient and higher velocities upstream and along the rerouted channel (USGS, 2004 and USDA, 2004) and are expected to flush residuals in the former powerhouse discharge channel downstream and erode bank material in the area of the Mill. Thus, the scope of the TCRA activities included actions or occurrences that threatened releases of waste material (as defined in the CD) from both the 12th Street Landfill and the Plainwell Mill properties. Since any such release may present an immediate threat to public health or welfare of the environment, Weyerhaeuser was authorized to conduct several emergency response actions in conjunction with completing the required work under the CD.

The U.S. EPA requires that all environmental monitoring and measurement efforts mandated or supported by the U.S. EPA participate in a centrally managed quality assurance program. Any party generating data under this program has the responsibility to implement minimum procedures to ensure that the precision, accuracy, completeness, and representativeness of the data are known and documented. To ensure that this responsibility is met uniformly, a written Quality Assurance Project Plan (QAPP) must be prepared for each project.

This Multi-Area QAPP presents the objectives, organization, functional activities, and specific quality assurance (QA) and quality control (QC) activities associated with implementing the projects that are described in Section 2. This QAPP also describes the specific protocols that will be followed for sampling, sample handling and storage, chain-of-custody, and laboratory analysis. This Multi-Area QAPP will be modified in the future as other sampling programs are identified or defined (*e.g.*, additional worksheets, such as Problem Definition-DQOs [Worksheet No. 10], will be inserted to describe the project sampling objectives and sampling program).

1.1 DEVELOPMENT OF THE MULTI-AREA QAPP

This QAPP has been prepared in accordance with the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP), Manual V1, March 2005 (U.S. EPA, 2005a), and the Uniform Federal Policy for Quality Assurance Project Plans, Part 2B, Quality Assurance/Quality Control (QA/QC) Compendium: Minimum QA/QC Activities V1, March 2005 (U.S. EPA, 2005b).

All QA/QC procedures performed under this QAPP will be in accordance with applicable professional technical standards, U.S. EPA requirements, other pertinent government regulations and guidelines, and the specific project goals and requirements.

1.2 PROJECT SETTING

The Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund site is located in southwestern Michigan. The site includes five disposal areas, five paper mill properties, an approximately 80-mile stretch of the Kalamazoo River from Morrow Dam to Lake Michigan, and a 3-mile stretch of Portage Creek. The primary site contaminant is PCBs,

a hazardous substance and probable human carcinogen. PCBs were introduced to Portage Creek and the Kalamazoo River through past discharges and disposal of PCB-contaminated residuals.

The 12th Street Landfill and Plainwell Mill sites are located in Allegan County, Michigan (Figure 1-2). The 12th Street Landfill is located in Otsego Township (Section 24, Township 1N, Range 11W), and the Plainwell Mill is located in the City of Plainwell (Section 30, Township 1N, Range 11W). Both sites are located adjacent to the Kalamazoo River, with the 12th Street Landfill located approximately 1½ miles northwest and downstream of the Plainwell Mill site. The 12th Street Landfill site encompasses approximately 6.5 acres and is situated on roughly a 24-acre property that is bordered to the east by woodlands and a former hydroelectric powerhouse discharge channel on the Kalamazoo River, to the north and west by wetlands, to the south and southwest by a asphalt plant mining operation, and to the south and southeast by industrially developed lands and the Plainwell Dam (which is scheduled to be removed as part of the U.S. EPA-approved TCRA in 2007-2008). The Plainwell Mill site encompasses approximately 36 acres and is bordered by the Kalamazoo River to the north, the Plainwell central business district to the east, residential properties to the south, and commercial properties and the City of Plainwell wastewater treatment plant to the west.

Plainwell, Inc., is the current owner of the 12th Street Landfill property, although Plainwell, Inc., is a bankrupt entity with no ongoing business operations. Weyerhaeuser is currently in negotiations with Plainwell, Inc., to take ownership of the 12th Street Landfill property. The mill property has been vacant since the former Simpson Plainwell Paper Company filed for bankruptcy in 2000. The City of Plainwell is the current owner of the Plainwell Mill property, having purchased the property out of the Plainwell Mill bankruptcy in 2006. Weyerhaeuser owned and operated the mill and the landfill for approximately a 9-year period, between 1961 and 1970. During that time, dewatered sludge from wastewater treatment operations was excavated from lagoons on the mill property and transported for disposal at the 12th Street Landfill site.

1.3 APPLICABILITY OF THE MULTI-AREA QAPP

This Multi-Area QAPP is applicable for work to be performed by Weyerhaeuser and its representatives within the Allied Paper, Inc./Portage Creek/Kalamazoo River

Superfund site. The work activities will include tasks conducted by Weyerhaeuser under its 2005 CD with the U.S. EPA, as may be amended or modified, at the following sites:

1. 12th Street Landfill (Operable Unit No. 4)
2. Plainwell Mill (Operable Unit No. 7)

Additional areas may be addressed in the future through modifications of this Multi-Area QAPP. This QAPP may be updated to address additional emergency activities and/or to integrate applicable workplan activities as required under the CD.

In September 2007, this QAPP was amended to include the removal of residuals and sediment along certain sections of the banks along the Plainwell Mill property. As defined in the 2005 CD, the limits of the Plainwell Mill Operable Unit (OU-7) extend to the top of the riverbank. Consequently, the banks of the mill property are part of the Kalamazoo River Operable Unit (OU-5).

In June 2009, the QAPP was amended to include the sampling and analysis activities associated with the Phase II RI Work Plan at the Plainwell Mill and the removal of paper residuals from outside of the landfill footprint as part of the Remedial Action (RA) at the 12th Street Landfill. At that time modifications were made to the QAPP to reflect the change in Project Coordinator as defined in the 2005 CD from RMT to Conestoga-Rovers & Associates (CRA).

2.0 SCOPE OF ACTIVITIES

The subsections below provide a summary of the scope for each project conducted under this Multi-Area QAPP to date, as well as new projects being added in this version. These projects include the following:

1. Emergency response activities in the former powerhouse discharge channel at the 12th Street Landfill (as described in Revision 00, June 2007, and Revision 01, August 2007)

2. Emergency Response activities on portions of the riverbank along the Plainwell Mill (as described in Revision 02, Addendum 01, September 2007)

3. Predesign investigations for the remedial design for the 12th Street Landfill (~~added in this version of the Multi-Area QAPP [i.e.,~~ as described in Revision 02, Addendum 02, February 2008])

4. RI/FS activities at the Plainwell Mill (as described in Revision 02, Addendum No. 3, November 2008, and updated in Revision 03, Addendum No. 4, June 2009)

5. Remedial Action Implementation activities at the 12th Street Landfill (added in this update to the Multi-Area QAPP, Revision 03, Addendum No. 4, June 2009).

The summaries of projects included in previous versions of this document have not been revised or deleted. As new projects are initiated, new information will be added to this Multi-Area QAPP to cover the new projects, and a new addendum number will be assigned to the document (*e.g.*, Addendum 02 will be updated to Addendum 03, and so on). If information included in a previous version of this document is changed, a new revision number will be assigned (*e.g.*, Revision 02 will be updated to Revision 03, and so on).

2.1 EMERGENCY RESPONSE ACTIVITIES AT THE 12TH STREET LANDFILL (OPERABLE UNIT NO. 4)

Weyerhaeuser has not yet received a formal notification from the U.S. EPA to proceed with the 12th Street Landfill RD/RA work specified in the CD. The full scope of the RA

for the 12th Street Landfill generally includes the excavation of wastewater residuals present outside the footprint of the landfill (on adjacent properties and in the former powerhouse discharge channel); the relocation of the excavated material back into the landfill, the construction of a landfill cover and erosion protection measures, and various environmental monitoring activities. Among the paper residuals to be excavated are those present in the former powerhouse discharge channel (a backwater of the Kalamazoo River), to the extent that these residuals are visibly contiguous with the landfill.

The TCRA in the Former Plainwell Impoundment includes the removal of the earthen section of the Plainwell Dam. The TCRA was approved by the U.S. EPA in February 2007, and the specified work will be implemented by the Kalamazoo River Study Group (KRSG) in 2007 and 2008 (Arcadis BBL, 2007a). Consequently, Weyerhaeuser needs to conduct certain activities at the 12th Street Landfill site under Section XVII, paragraph 67 (Emergency Response), of Weyerhaeuser's CD with the U.S. EPA in order to accommodate the TCRA and to prevent erosion of the banks of the landfill. These activities include removing visible residuals in the former powerhouse discharge channel, cutting back the existing landfill slope along the river, and installing erosion protection on the eastern bank of the 12th Street Landfill consistent with the requirements of the Record of Decision (ROD).

2.1.1 FORMER POWERHOUSE DISCHARGE CHANNEL

The 12th Street Landfill is situated directly downstream of the Plainwell Dam, on the same side of the river as the earthen section of the dam that will be removed as part of the TCRA. After the earthen section of the Plainwell Dam is removed, the former powerhouse discharge channel (currently a backwater) will become the main channel of the Kalamazoo River. This will create a larger gradient on the river with resultant higher flow velocities and greater shear stresses (*i.e.*, erosion potential) in the former powerhouse discharge channel and on various bank areas upstream of the current Plainwell Dam. The change will also alter flood conditions near the landfill. Without action, the channel rerouting will resuspend and redistribute paper residuals that are present in the discharge channel, including residuals that may be contiguous with the 12th Street Landfill. The modified flow is also modeled to increase shear stresses along the riverbank adjacent to the 12th Street Landfill, resulting in possible destabilization of

the banks and increased erosion. To prevent this from occurring, Weyerhaeuser plans to perform the following activities:

- Conduct bathymetric and visual sediment assessments to determine the visual characteristics of the sediment and the depth of water in the former powerhouse discharge channel (RMT, 2007a). Use this information, in conjunction with previously available information (G&M, 1994; U.S. EPA, 2004), to estimate the extent of visual wastewater residuals that are contiguous with the 12th Street Landfill, present in the channel sediment, and subject to mobilization once the Kalamazoo River is rerouted.
- Excavate visible wastewater residuals that are contiguous with the 12th Street Landfill and present in the channel sediment. Dewater the sediment, and treat and sample water from the dewatering process before discharge back to the Kalamazoo River. Dispose the excavated sediment in the 12th Street Landfill.
- Collect post-excavation confirmation samples in the former powerhouse discharge channel to confirm that wastewater residuals that are visibly contiguous with the landfill have been removed, and that PCB concentrations in the excavated area are below 4 mg/kg.

The locations and concentration ranges of data collected previously at the site, as well as an indication of whether residuals were observed, are illustrated on Figure 2-1.

2.1.2 EASTERN BANK OF THE LANDFILL

As stated in Subsection 2.1.1, after the earthen section of the Plainwell Dam is removed, the former powerhouse discharge channel will become the main channel of the Kalamazoo River. This will create higher velocities and greater shear stresses (*i.e.*, erosion potential), as well as altered flood conditions along the eastern bank of the 12th Street Landfill. Without action, the channel rerouting could erode mixed fill/paper residuals at the toe of the eastern landfill bank and may lead to instability of the bank. Moreover, certain components of the ROD, such as cutting back the sideslope of the landfill along the river and creating space for an access road along the river, are more effectively and efficiently implemented in conjunction with the work in the former discharge channel. Consequently, Weyerhaeuser plans to perform the following

activities that are required by the ROD for the 12th Street Landfill as part of an Emergency Response Action:

- Cut back the existing slope of the 12th Street Landfill along the river to create a more stable angle and to provide a buffer zone to ensure that, once the final cover system is installed, there is no direct contact between the paper residuals in the landfill and the Kalamazoo River/former powerhouse discharge channel, and to provide space for an access road along the riverfront. The excavated mixed fill/paper residuals from the eastern bank will be disposed in a designated area on top of the 12th Street Landfill.
- Install erosion protection on the newly graded eastern bank of the landfill to provide protection from a 500-year flood event.

Geotechnical borings have been installed in preparation for this work (RMT, 2007b). Consistent with the requirements of the ROD, no environmental samples are planned in connection with the above work at the 12th Street Landfill.

The final cover over the landfill, along with the other components of the landfill remedy, will be designed and installed in a manner and time frame consistent with the CD.

2.2 EMERGENCY RESPONSE ACTIVITIES AT THE FORMER PLAINWELL MILL BANKS (OPERABLE UNIT NO. 5)

Weyerhaeuser has been authorized by the U.S. EPA to conduct Emergency Actions at two separate locations adjacent to the Kalamazoo River under Paragraph 67 of their 2005 CD. As part of the Emergency Action for the former powerhouse channel at the 12th Street Landfill (Operable Unit 04), Multi-Area QAPP and Field Sampling Plan (FSP) were submitted and approved (approval letter from Michael Berkoff, dated July 24, 2007). On June 29, 2007, the U.S. EPA also authorized Weyerhaeuser to take actions to prevent, abate, or minimize a release or potential release of hazardous substances from the former Plainwell Mill banks. The former Plainwell Mill banks are considered part of the Kalamazoo River operable unit (Operable Unit 05).

The following objectives have been developed for the Emergency Action along the former Plainwell Mill banks:

- Remove or contain visible paper residuals and address previously identified areas of reported PCBs concentrations of greater than 50 mg/kg in soils/sediments along the former Plainwell Mill banks to a target concentration of 4 mg/kg.
- Reconstruct bank, as needed, to minimize future release of PCBs.
- Reconfigure bank to limit upland cutbacks into former Plainwell Mill property and place erosion controls to provide comparable stability to pre-excavation conditions.

To achieve the excavation objectives stated above, physical and analytical data from previous investigations performed on sediments, bank soils, and floodplain soils were reviewed to identify and delineate specific areas of sediment and soil to be targeted as part of this Emergency Action. The design approach to the Emergency Action is presented in a draft final Plainwell Mill Banks Emergency Action Design Report (RMT, 2007c). Site preparation work is scheduled to begin late September 2007 with construction to follow in early October. The 2,600 linear feet of bank length has been divided into four zones based upon physical conditions and estimated quantity of visual residuals targeted for excavation. These construction zones will facilitate construction by providing an opportunity to refine the construction approach and schedule between each zone.

2.3 PREDESIGN INVESTIGATIONS FOR THE REMEDIAL DESIGN FOR THE 12TH STREET LANDFILL (OPERABLE UNIT NO. 4)

The 12th Street Landfill, composed primarily of the 6.5-acre closed landfill and the four areas outside the landfill where PCB-contaminated residual material has been observed, is Operable Unit No. 4 (OU-4) of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site (Kalamazoo River Superfund Site). The landfill is situated with 17 acres of wetlands on an approximately 24-acre parcel. Additional portions of OU-4 that are located outside the landfill property include the woodland area owned by the State of Michigan (State) under the management of the Michigan Department of Natural Resources (MDNR), the asphalt plant operation adjacent to the landfill, and the former powerhouse discharge channel. Contamination in the former powerhouse discharge channel was addressed as part of Emergency Actions implemented in 2007.

Paper residuals from the former Plainwell Mill (mill), located in Plainwell, Michigan, were disposed in the 12th Street Landfill during the period from approximately 1955 to 1983. The landfill reportedly also accepted solid waste from the mill during part of its period of active operation. A number of investigations have been performed at the site. The investigations have confirmed the nature of the material in the landfill and have shown that paper residuals are present in certain areas outside of the landfill (*i.e.*, in the wetlands to the north/northwest, the asphalt plant property, and the State property). Some of the residuals/native soil beyond the toe of the landfill (*i.e.*, outside the footprint of the landfill) may contain PCBs at concentrations exceeding State of Michigan or Kalamazoo River Superfund Site-specific ecological risk-based criteria.

A ROD for OU-4 was issued on September 28, 2001. The major components of the selected remedy include the following: "(1) the excavation and relocation into the landfill of contaminated residuals currently in the woodland, wetlands, and adjacent property, and the residuals in the former powerhouse discharge channel that are contiguous with the eastern side of the landfill, followed by the construction of a containment system; (2) the excavation and relocation into the landfill of the east side of the landfill along the former powerhouse discharge channel to create a buffer zone sufficient to insure no hydraulic connection between the wastes within the landfill containment system and the Kalamazoo River or the former powerhouse discharge channel; (3) the restoration of areas excavated, cleared and grubbed, or otherwise affected by the remedial action; (4) the construction of a side wall containment system around the outside of the landfill; (5) the construction of a cover (cap) over the landfill; (6) the installation of an appropriate groundwater monitoring network and the performance of long-term groundwater monitoring; (7) the performance of short-term surface water monitoring; (8) the placement of deed restrictions; (9) the construction of a fence, permanent markers, and warning signs; (10) the investigation of the need for a leachate collection system and, if deemed necessary, the construction of a leachate collection system; and (11) the implementation of long-term maintenance and post-closure care."

In January 2005, Weyerhaeuser negotiated a CD with the U.S. EPA (Civil Action No. 1:05-CV0003) for the design and implementation of certain response actions at Operable Unit #4 and the Plainwell, Inc., Mill. These actions include the RD/RA activities for the 12th Street Landfill. This revision of the Multi-Area QAPP has been

prepared in fulfillment of the requirements for an RD Workplan for the 12th Street Landfill that are contained in the CD and the SOW.

The RD Workplan for the 12th Street Landfill includes a number of predesign investigations, some of which will involve field data collection and visual observations. Field data collection activities will include visual information obtained by the advancement of test pits, visual information obtained by the advancement of Geoprobe® borings, and gas concentration measurements (methane, carbon dioxide, and oxygen) in existing monitoring wells and in the Geoprobe® borings advanced as part of the predesign investigation.

The field investigations will involve: 1) a determination of the extent of visible paper residuals beyond the landfill footprint, 2) the collection of data to support the grading design for the final landfill cover, and 3) the collection of data for use in the design of a landfill gas venting system. Sufficient information is available from previous investigations to evaluate the potential need for a leachate collection system. No additional field information is needed to support this objective.

2.3.1 EXTENT OF PAPER RESIDUALS BEYOND LANDFILL FOOTPRINT

The objectives of this investigation include the following:

Wetland

- To confirm the approximate areal extent of visible paper residuals beyond the toe of the landfill as delineated based on the results from previous investigations.
- To assess the degree of difficulty in distinguishing the visible paper residuals from the native soil.
- To evaluate potential constructability issues associated with working in the wetland north of the landfill.

Asphalt Plant/State Properties

- To delineate the areal extent, and to better estimate the depth, of visible paper residuals on the asphalt plant property to the southwest and on the State property to

the southeast, in order to support discussions with owners of these adjacent properties concerning access for conducting the remedial actions on the properties required by the ROD.

The general scope of the predesign investigation includes the following activities:

Wetland

- Excavate approximately three test pits at the locations depicted on Figure 2-2. The test pits are anticipated to be approximately 10 to 15 feet long (perpendicular to the edge of the landfill) and approximately 2 to 4 feet wide. The test pits will be excavated to a maximum depth of 3 feet if no paper residuals are visually apparent, or to the bottom of visually-identifiable residuals.

Asphalt Plant/State Properties

- Excavate approximately three test pits on the asphalt plant property, and approximately four test pits on the State property at the locations depicted on Figure 2-2. The test pits are anticipated to be approximately 10 to 15 feet long (perpendicular to the edge of the landfill) and approximately 2 to 4 feet wide. The test pits will be excavated to a maximum depth of 3 feet if no paper residuals are visually apparent, or to the bottom of visually-identifiable residuals.

  In the event that in-field conditions limit the use of test pit excavating equipment (*e.g.*, a backhoe), other tools, such as hand augers or shovels, may be used instead. In such instances, the U.S. EPA project manager, or designated alternate, will be contacted to discuss the situation and to agree on a course of action. In addition, Weyerhaeuser will conduct a kick-off meeting with the U.S. EPA and its field representative(s) at the outset of the predesign field investigation. During this meeting, the schedule for conducting the predesign field activities and the process for obtaining U.S. EPA approval of field modifications will be reviewed.

2.3.2 GRADING DESIGN

The objective of this investigation is the following:

- To better estimate the depth of the paper residuals along the property boundaries with 12th Street, the asphalt plant to the southwest, and with the State property to the southeast, in order to reduce uncertainties in designing the final landfill grades.

The general scope of this investigation is the following:

- Advance approximately nine Geoprobe® borings into the 12th Street Landfill at locations where fill material is believed to extend beyond the property boundaries to the southwest and to the southeast (see locations on Figure 2-3). The borings will be advanced approximately 5 feet into the native soil underlying the fill, or to refusal.
- Advance a minimum of two soil borings (RDB-10 and RDB-11) near the southern end of the landfill, as shown on Figure 2-3, to confirm the thickness of the fill in this area. Advance the borings approximately 5 feet into the native soil underlying the fill or to refusal. The locations of these borings may be adjusted in the field as necessary to avoid underground or aboveground utility lines. Additional borings may be installed to the north of the initial borings as may be deemed useful by Weyerhaeuser, in consultation with oversight agencies as needed, for purposes of designing the landfill cover (*e.g.*, if fill material is not encountered at a location where existing data indicate that fill is present).

2.3.3 LANDFILL GAS MANAGEMENT

The objective of this investigation is the following:

- To collect readily accessible information about the subsurface landfill gas conditions at the 12th Street Landfill that may be useful in designing a passive gas venting system for the 12th Street Landfill.

The general scope of this field investigation is the following:

- Measure the concentrations of methane, carbon dioxide, and oxygen in the existing groundwater monitoring wells at the 12th Street Landfill that are screened in the

vadose zone (MW-6A, MW-7A, and MW-8A), and in the Geoprobe® boreholes used to estimate the depth of the paper residuals along the property boundaries (see locations on Figure 2-3). Pressures that may have developed within the groundwater monitoring wells caused by excess landfill gas (if present) will also be measured. A passive gas venting system can be designed without the above information. If these data cannot be readily obtained, additional efforts will not be employed to collect the information.

2.4 RI/FS AT THE PLAINWELL MILL (OPERABLE UNIT NO. 7)

2.4.1 PHASE 2 OF ADDENDUM NO. 1

In a letter to Weyerhaeuser dated February 19, 2008, the U.S. EPA requested additional work along the former Plainwell Mill banks in response to discovery of elevated concentrations of PCBs and oily soil encountered along the Plainwell Mill banks during the separate Plainwell Mill Banks Emergency Response activities. On July 15, 2008, a Draft Phase 2 Addendum No. 1 to the Plainwell Mill RI/FS Work Plan was prepared and provided to U.S. EPA for review. The U.S. EPA provided technical review comments on the Draft Phase 2 Addendum No. 1 in a letter dated July 31, 2008. Subsequently, Weyerhaeuser provided response to comments and a redlined version of the Work Plan Addendum in a letter dated August 8, 2008. The Phase 2 of Addendum No. 1 Work Plan has been designed to meet the following objectives:

1. Identify Source: Identify, as much as possible, a likely cause of the oily sheen observed near the former transformer pad, with focus on the possible presence of NAPL.
2. Determine Relationships: Determine if there is a relationship between the oily material near the transformer pad and the elevated PCB concentrations found at PM-SD-041, PEX-1, and PEX-2 (Figure 2).
3. Assess NAPL: Determine whether NAPL, if present, is entering the Kalamazoo River.
4. Define Nature of Contamination: Determine if the oily material present in soils and fill near the transformer pad and at locations PM-SD-041, PEX-1, and PEX-2 contain petroleum products and/or PCBs.

5. Develop Next Steps: Determine immediate actions needed and how the next phase of investigation should be integrated with other RI activities.

Due to the nature of the investigate areas likely to contain fill material and or construction debris, test pits have been selected as the best method for successful site characterization. Test pits will be advanced to either native soils or the water table using an excavator taking care to minimize site disturbances to the extent practical. Additional details and the rationale for the proposed test pit investigation are presented in the Phase 2 of Addendum No. 1 Work Plan and the associated QAPP Worksheet #10-4.

2.4.2 PLAINWELL MILL RI/FS – PHASE I INITIAL GROUNDWATER ASSESSMENT

The Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment includes a collection of shallow groundwater samples to assess the possible presence of floating product and to quantify the concentrations of constituents in shallow groundwater that may have been contributed by suspected or known contamination present on site. The Plainwell Mill is located at 200 Allegan Street in Plainwell, Michigan. The limited existing groundwater data, the generally permeable subsurface sands present along the Kalamazoo River, the site history, and the size and configuration of the Plainwell Mill property make a phased groundwater investigation especially useful for focusing future data collection activities needed to meet the overall objectives of the required RI/FS.

The specific objectives for the Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment are:

- To determine if free product is present on the groundwater table at the monitoring well locations.
- To evaluate shallow groundwater quality across the Plainwell Mill property.
- To assess shallow site-specific hydro-geologic characteristics that will be used to refine the current site conceptual model.
- To determine the potential usability of past site data in the determination of the nature and extent of contamination present on the Plainwell Mill.

- To identify data gaps that need to be addressed during Phase II investigations of soil and groundwater.

Groundwater sampled from each location will be analyzed for volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), Resource Conservation and Recovery Act (RCRA) metals, and PCBs. As a frame of reference, concentrations of measured constituents will be compared to applicable Michigan standards.

The results of this phase of the RI will also be used to help assess the potential usefulness of groundwater results from previous environmental assessments conducted on the site, better define site conditions, and then allow identification of data gaps. The identified data gaps will then be addressed during the Phase 2 soil and groundwater sampling activities expected for this site. Additional details and the rationale for the phased groundwater assessment are presented in the Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment Work Plan and the associated QAPP Worksheet #10-4.

2.4.3 PHASE II RI WORK PLAN

Weyerhaeuser provided the U.S. EPA with a Phase II RI Work Plan for the Plainwell Mill on May 20, 2009. A formal notification from the U.S. EPA to proceed with implementation of the Work Plan has not been received yet.

The Phase II RI Work Plan investigation was developed to meet the following objectives:

- Perform a supplemental groundwater investigation, developed based on the results of the Phase I RI groundwater investigation to further evaluate the nature and extent of impacts to groundwater and their potential sources;
- Further assess shallow, site-specific hydrogeologic characteristics and interconnections with the Kalamazoo River; and
- Perform soil investigations in the former wastewater sludge and dewatering lagoon and aeration basin area, the area of the mill buildings, and the north central portion of the Plainwell Mill, to adequately characterize the nature and extent of impacts to soil in the unsaturated zone that may have occurred due to historical operations.

To facilitate the evaluation of the historical information, Plainwell Mill has been divided into three areas based on their locations and noted historical environmental impacts. The three areas are the former wastewater sludge dewatering lagoons and aeration basin (Area 1), mill building area (Area 2), and north central portion area of the Plainwell Mill (Area 3). Based on the review of the historical documentations, the following general scope of investigation has been developed to determine the potential impacts associated with historical activities and provide a complete assessment of the Plainwell Mill:

- Area 1:
  - Installation of deep soil borings to ensure that a minimum of one deep soil boring with appropriate sample intervals is available for each lagoon location;
  - Verification sampling at locations that exceedances noted during historical investigations and further characterization of soil chemistry across the lagoon area as needed to meet the objectives of the RI;
  - Investigation of any potential impacts associated with the aeration basin;
  - Installation of one monitoring well screened within the paper waste in the lagoons to determine contaminate concentrations of the waste for comparison to the historical analytical data;
  - Re-installation of an existing monitoring well located south west of the lagoon areas to characterize groundwater flow direction through this area and provide an alternate background monitoring well location;
  - Installation of a monitoring well north of the former secondary clarifier to determine any potential groundwater impacts related to prior discharges;
  - Soil sampling during installation of the new monitoring wells to characterize potential soil impacts at these areas; and
  - Sampling of current and new monitoring wells to determine and confirm groundwater impacts.

- Area 2 :
  - Collection of soil samples from potential contamination areas surrounding the historical transformer pad located in the north east portion of this area adjacent to the Kalamazoo River;
  - Potential surficial soil sampling following visual inspection of outflow points identified during previous investigations along the Kalamazoo

River to ensure capping was conducted properly and no further issues pertain to these outflows;

- Potential surficial soil sampling following the visual inspection of the surface soils surrounding the building for presence of any staining in relation to the historical activities;
- Potential collection of soil samples following installation of one soil boring in the southern corner of the parking lot area adjacent to the Mill Race for visual inspection;
- Installation of one monitoring well in the southeast portion of this area to determine influence of the Mill Race on the water levels at the southern property boundary;
- Installation of a monitoring well adjacent to the mill building near the end of the Mill Race to further define the groundwater flow patterns at this area; and
- Collection of groundwater samples from existing and new monitoring wells to confirm the groundwater chemistry.

- Area 3:
  - Collection of soil samples from historical locations of historical exceedances to confirm existing analytical data;
  - Installation of one monitoring well to replace an existing monitoring well that has been damaged beyond repair to confirm groundwater exceedances previously noted at the monitoring location;
  - Installation of eight soil borings in the vicinity of the former Coal Pile Storage area to further define the potential subsurface coal contamination within this area and determine the locations of any potentially contaminated soils;
  - Collection of groundwater samples from existing and new monitoring wells to confirm the groundwater chemistry at this area;
  - Installation of four soil borings in the vicinity of the 200,000 gallon Fuel Oil Tank to further define any impacts related to soil contamination around the fuel tank; and
  - Installation of one monitoring well to confirm previous groundwater results noted in this area in the vicinity of the No. 6 Fuel Tank Area.

Collected soil samples will be analyzed for Target Compound List (TCL) VOCs, TCL SVOCs, PCBs, Target Analyte List (TAL) metals as defined in this QAPP, Synthetic Precipitation Leaching Procedure (SPLP) metals, and general chemistry parameters. Collected groundwater from monitoring locations will be analyzed for TCL VOCs, TCL SVOCs, PCBs, and TAL inorganics. In addition two surface water samples will be collected and analyzed for low level mercury, methyl mercury, and hardness. The results of these sampling activities will be used to demonstrate compliance with the Michigan Part 201 Generic Residential Cleanup Criteria (GRCC) pursuant to the MDEQ's Sampling Strategies and Statistics Training Materials for Part 201 Cleanup Criteria (STM; MDEQ, 2002).

2.5 REMEDIAL ACTION WORK PLAN AT 12TH STREET LANDFILL (OPERABLE UNIT NO. 4)

Weyerhaeuser submitted the Pre-Final Design Report – Addendum No. 1 to the U.S. EPA on May 27, 2009 for the 12th Street Landfill Operable Unit No. 4. The RA Work Plan will be submitted once the U.S. EPA has reviewed the Pre-Final Design Report Addendum No. 1. The scope of the RA for the 12th Street Landfill includes excavation of paper residuals present outside the footprint of the landfill (on adjacent properties), landfill grading, the construction of a landfill cover and erosion protection measures, and surface water management, landfill gas management, construction of access road, abandonment of existing groundwater monitoring wells, installation of groundwater monitoring wells, and various environmental monitoring activities.

2.5.1 EXCAVATION ACTIVITIES

The areal limits of visible paper residuals outside the footprint of the landfill on the MDNR property, the asphalt plant property, and in the wetlands were previously delineated based on information obtained by Geraghty and Miller and the U.S. EPA in 1994 and 2003, respectively (G&M, 1994b and U.S. EPA, 2004), and have been refined based on the findings of the predesign investigation performed by Weyerhaeuser in 2008. Sufficient information is available from previous investigations to implement the excavation activities. Upon completion of the excavation activities on the MDNR property and the asphalt plant property to the visual extent of the distinguishable paper residuals, samples of the native soil underlying the excavated paper residuals at the base

of the excavation will be collected and analyzed to confirm the adequacy of the excavation activities. Collected soil samples will be analyzed for PCBs. In addition samples collected from asphalt plant property will be analyzed for VOCs.

This verification sampling will be used to demonstrate completion with the Michigan Part 201 GRCC pursuant to the MDEQ's Sampling Strategies and Statistics Training Materials for Part 201 Cleanup Criteria (STM; MDEQ, 2002).

3.0 DOCUMENT OVERVIEW

This Multi-Area QAPP has been developed in accordance with the UFP-QAPP guidance (U.S. EPA, 2005a), which is composed of a series of 37 worksheets, along with a series of attachments. The worksheets provide information on project management, project objectives, measurement and data acquisition, project assessment and oversight, and data review. The attachments include chain-of-custody records, laboratory certifications, laboratory quality assurance plans, and laboratory standard operating procedures (SOPs). In accordance with the U.S. EPA guidance, cross-referencing is utilized where applicable, in order to streamline the document. This includes providing references to planning documents that are companion documents to this Multi-Area QAPP.

4.0 REFERENCES

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WORKSHEETS

QAPP Worksheet #1
Title and Approval Page

Site Name/Project Name:	Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site
Site Location:	Kalamazoo and Allegan Counties, including (but not limited to) 3 miles of Portage Creek and the Kalamazoo River from the City of Kalamazoo to Lake Michigan ▪ Operable Unit No. 4 - 12th Street Landfill ▪ Operable Unit No. 7 - Plainwell Mill
Document Title:	Multi-Area Quality Assurance Project Plan, Weyerhaeuser Company
Lead Organization:	U.S. EPA Region 5
Preparer's Name and Organizational Affiliation:	Gregory A. Carli, P. E., CRA
Preparer's Contact Information:	261 Martindale Road, Unit#3, St. Catharines, ON L2W 1A2 gcarli@craworld.com
Preparation Date: (1) Revision 03, Addendum No. 4 represents change in Project Coordinator from RMT to CRA and only includes worksheets relevant to CRA activities	Revision 00-June 2007 Revision 01-September 2007 (*i.e.*, Addendum) Revision 02-February 2008 Revision 02, Addendum 2 - September 2008 Revision 02, Addendum 3–November 2008 Revision 03, Addendum 4–June 2009
Investigative Organization's Project Manager For Investigative Activities at the Plainwell Mill (Operable Unit No. 7):	Signature: _____ Gregory Carli, CRA
Investigative Organization's Project Manager For Investigative Activities at the 12th Street Landfill (Operable Unit No. 4):	Signature: _____ Gregory Carli, CRA
Investigative Organization's QA Officer:	Signature: _____ Paul Wiseman, CRA
Lead Organization's Program Manager for the 12th Street Landfill (Operable Unit No. 4):	Signature: _____ Michael Berkoff, U.S. EPA Region 5
Lead Organization's Program Manager for the Plainwell Mill (Operable Unit No. 7):	Signature: _____ Sam Chummar, U.S. EPA Region 5

Document Control Number: 56394 (3)-001

QAPP Worksheet #2
Identifying Information

Site Name/Project Name:	Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site
Site Location:	Kalamazoo and Allegan Counties, including (but not limited to) 3 miles of Portage Creek and the Kalamazoo River from the city of Kalamazoo to Lake Michigan ▪ Operable Unit No. 4 - 12th Street Landfill ▪ Operable Unit No. 7 - Plainwell Mill
Site Number/Code:	MID006007306
Operable Unit:	Operable Units No. 4 and 7
Contractor's Name:	NA
Contractor's Number:	NA
Contract Title:	NA
Work Assignment Number:	NA
Identify guidance used to prepare QAPP:	Uniform Federal Policy for Quality Assurance Project Plans, Manual VI (U.S. EPA, 2005a)
Identify regulatory program:	Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)
Identify approval entity:	U.S. EPA Region 5
Indicate whether the QAPP is a generic or a project-specific QAPP:	This is a project-specific Multi-Area QAPP for Remedial Action implementation at the 12th Street Landfill (Operable Unit No. 4) and the Remedial Investigation activities at the Plainwell Mill (Operable Unit No. 7). This QAPP will be updated as required for future work at the 12th Street Landfill Site and Plainwell Mill.
List dates of scoping sessions that were held:	Emergency Activities for the 12th Street Landfill: May 8, 2007, and June 6, 2007, at U.S. EPA Region 5 offices in Chicago, Illinois Emergency Activities for the Plainwell Mill Banks: August 14, 2007, Submittal of conceptual design approach and follow-up discussions regarding U.S. EPA comments Predesign Investigations for the RD for the 12th Street Landfill: December 7, 2007, at U.S. EPA Region 5 offices in Chicago, Illinois, and on January 9, 2008, via conference call.

QAPP Worksheet #2
Identifying Information

List dates of scoping sessions that were held (Continued):	Work Plan preparation and comment discussion for Phase 2 of Addendum No. 1 and Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment: July 16, 2008, July 22, 2008 via conference call. Plainwell Mill RI Work Plan preparation and submittal of Phase II RI Work Plan, May 20, 2009 and related follow up discussions on June 17, 2009. 12th Street Landfill Design medications as presented in CRA memorandum to U.S. EPA dated April 23, 2009; Pre-Final Design Report Addendum No. 1 (May 27, 2009) and related conference calls on April 17, 2009 and May 1, 2009.
List dates and titles of QAPP documents written for previous site work, if applicable:	
Quality Assurance Project Plan, organization partners (stakeholders), and connection with lead organization:	**(Site-Wide QAPP)** Blasland & Bouck Engineers, P.C. 1993. Quality Assurance Project Plan, June 1993. Prepared on behalf of the Kalamazoo River Study Group (KRSG). Approved by the U.S. EPA Region 5 and the Michigan Department of Natural Resources (MDNR). Other stakeholders included the Michigan Department of Environmental Quality (MDEQ), the United States Fish & Wildlife Service, and the National Oceanic & Atmospheric Administration. **(Operable Unit No. 7)** RMT, 2006. Draft Quality Assurance Project Plan for the Remedial Investigation/Feasibility Study – Plainwell Mill, September 2006. Prepared on behalf of Weyerhaeuser Company. Project stakeholders include the MDEQ and the City of Plainwell. **(Site-Wide QAPP)** RMT, Rev. 02, Addendum 3, 2008. This Multi-Area QAPP prepared on behalf of Weyerhaeuser and its representatives within the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site. Stakeholders include the U.S. EPA and the Michigan Department of Environmental Quality (MDEQ) with response pending. **(Site-Wide QAPP)** CRA, Rev. 03, Addendum 4, 2009 (current Addendum). This Multi-Area QAPP prepared on behalf of Weyerhaeuser and its representatives within the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site. This document addresses activities associated with the Phase II RI Work Plan at the Plainwell Mill and the removal activities associated with the Remedial Action (RA) at the 12th Street Landfill. Project stakeholders include the U.S. EPA and the Michigan Department of Environmental Quality (MDEQ) with response pending
List data users:	Weyerhaeuser Company, U.S. EPA Region 5

QAPP Worksheet #2
Identifying Information

Lead Organization's Program Manager:	**Operable Unit No. 4:** Michael Berkoff, U.S. EPA Region 5 Remedial Project Manager (RPM) **Operable Unit No. 7:** Sam Chummar, U.S. EPA Region 5 RPM

REQUIRED QAPP ELEMENT(S) AND CORRESPONDING QAPP SECTION(S) (U.S. EPA, 2005a)	REQUIRED INFORMATION	CROSSWALK TO RELATED INFORMATION AND DOCUMENTS
Project Management and Objectives		
2.1 Title and Approval Page	▪ Title and Approval Page	Worksheet #1, Title and Approval Page
2.2 Document Format and Table of Contents	▪ Table of Contents ▪ QAPP Identifying Information	The Table of Contents is provided following the QAPP cover page. Worksheet #2, Identifying Information
2.2.1 Document Control Format		
2.2.2 Document Control Numbering System		
2.2.3 Table of Contents		
2.2.4 QAPP Identifying Information		
2.3 Distribution List and Project Personnel Sign-Off Sheet	▪ Distribution List ▪ Project Personnel Sign-Off Sheet	Worksheet #3, Distribution List; and Worksheets #4-2 and #4-3, Project Personnel Sign-Off Sheet
2.3.1 Distribution List		
2.3.2 Project Personnel Sign-Off Sheet		
2.4 Project Organization	▪ Project Organizational Chart ▪ Communication Pathways ▪ Personnel Responsibilities and Qualifications Table ▪ Special Personnel Training Requirements Table	Worksheets #5-4 and 5-5, Project Organization Charts; Worksheet #6-4 and 6-5, Communication Pathways; Worksheet #7, Personnel Responsibilities and Qualifications; and Worksheet #8, Special Personnel Training Requirements
2.4.1 Project Organization Chart		
2.4.2 Communication Pathways		
2.4.3 Personnel Responsibilities and Qualifications		
2.4.4 Special Training Requirements and Certification		

QAPP Worksheet #2
Identifying Information

Project Management and Objectives (*Continued*)		
2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	▪ Project Planning Session ▪ Documentation (including Data Needs tables) ▪ Project Scoping Session Participants Sheet ▪ Problem Definition, Site History, and Background ▪ Site Maps (historical and current)	Worksheet #8, Special Personnel Training Requirements; Worksheets #9-6 and 9-7, Project Scoping Session Participants Sheet; and Worksheets #10-5 and 10-6, Problem Definition-DQOs Site history and more detail concerning the project DQOs can be found in the companion documents to this Multi-Area QAPP. Site maps can be found on Figures 1-1, 1-2, and 2-1 through 2-3.
2.6 Project Quality Objectives and measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement performance Criteria	▪ Site-Specific Project Quality Objectives (PQOs) ▪ Measurement Performance Criteria Table	Worksheets # 11-5 and 11-6, Project Quality Objectives/Systematic Planning Process Statements. Worksheets #12-1 through 12-17, Measurement Performance Criteria
2.7 Secondary Data Evaluation	▪ Sources of Secondary Data and Information ▪ Secondary Data Criteria and Limitations Table	Worksheets #13-1 and 13-2, Secondary Data Criteria and Limitations
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	▪ Summary of Project Tasks ▪ Reference Limits and Evaluation Table ▪ Project Schedule/Timeline Table	Worksheet #14, Summary of Project Tasks; Worksheets #15-1 through 15-4, Reference Limits and Evaluation; and Worksheet #16-5 and 16-6, Project Schedules/Timelines.

QAPP Worksheet #2
Identifying Information

Measurement/Data Acquisition		
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Container Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	▪ Sampling Design and Rationale ▪ Sample Location Map ▪ Sampling Locations and Methods/ SOP Requirements Table ▪ Analytical Methods/SOP Requirements Table ▪ Field Quality Control Sample Summary Table ▪ Sampling SOPs ▪ Project Sampling SOP References Table ▪ Field Equipment Calibration, Maintenance, Testing, and Inspection Table	Worksheet #17-5 and 17-6, Sampling Design and Rationale; Worksheet #18-4 and 18-5, Sampling Locations and Methods/SOP Requirements; Worksheet #19, Analytical SOP Requirements (sample containers, preservation, and holding times); Worksheet #20, Field Quality Control Sample Summary Worksheet #21, Project Sampling SOP Reference; and Worksheet #22, Field Equipment Calibration, Maintenance, Testing, and Inspection The laboratory SOPs can be found in Attachment 1-5. More details concerning the sampling design and rationale and the field sampling procedures can be found in the companion documents to this Multi-Area QAPP.
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	▪ Analytical SOPs ▪ Analytical SOP References Table ▪ Analytical Instrument Calibration Table ▪ Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	Worksheet #23, Analytical SOP References; Worksheet #24, Analytical Instrument Calibration; and Worksheet #25, Analytical Instrument and Equipment Maintenance, Testing, and Inspection The laboratory SOPs can be found in Attachment 1-5.
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample Handling and Tracking System 3.3.3 Sample Custody	▪ Sample Collection Documentation Handling, Tracking, and Custody SOPs ▪ Sample Container Identification ▪ Sample Handling Flow Diagram ▪ Example Chain-of-Custody Record and Seal	Worksheet #27, Sample Custody Requirements More details concerning the field sampling procedures can be found in the companion documents to this Multi-Area QAPP. Example COC forms can be found in Attachment 1-3.

QAPP Worksheet #2
Identifying Information

Measurement/Data Acquisition (*continued*)		
3.4 Quality Control Samples	▪ QC Samples Table ▪ Screening/Confirmatory Analysis Decision Tree	Worksheet #28-1 through #28-21. Present QC sample information for project analysis
3.4.1 Sampling Quality Control Samples		
3.4.2 Analytical Quality Control Samples		
3.5 Data Management Tasks	▪ Project Documents and Records Table ▪ Analytical Services Table ▪ Data Management SOPs	Worksheet #29, Project Documents and Records, and Worksheet #30, Analytical Services
3.5.1 Project Documentation and Records		
3.5.2 Data Package Deliverables		
3.5.3 Data Reporting Formats		
3.5.4 Data Handling and Management		
3.5.5 Data Tracking and Control		
4.1 Assessments and Response Actions	▪ Assessments and Response Actions ▪ Planned Project Assessments Table ▪ Audit Checklists ▪ Assessment Findings and Corrective Action Responses Table	Worksheet #31, Planned Project Assessments, and Worksheet #32, Assessment Findings and Corrective Action Responses The laboratory Quality Assurance Manual and Laboratory Policies and Guidelines documents can be found in Attachments 1-4 and 1-6, respectively.
4.1.1 Planned Assessments		
4.1.2 Assessment Findings and Corrective Action Responses		
4.2 QA Management Reports	▪ QA Management Reports Table	Worksheet #33, QA Management Reports
4.3 Final Project Report		

QAPP Worksheet #2
Identifying Information

Data Review		
5.1 Overview		
5.2 Data Review Steps	▪ Verification (Step I) Process Table ▪ Validation (Steps IIa and IIb) Process Table ▪ Validation (Steps IIa and IIb) Summary Table ▪ Usability Assessment	Worksheet #34, Verification (Step 1) Process; Worksheet #35, Validation (Step I) Process; Worksheet #36, Validation (Steps IIa and IIb) Summary; and Worksheet #37, Usability Assessment.
5.2.1 Step I: Verification		
5.2.2 Step II: Validation		
5.2.2.1 Step IIa Validation Activities		
5.2.2.2 Step IIb Validation Activities		
5.2.3 Step III: Usability Assessment		
5.2.3.1 Data Limitations and Actions from Usability Assessment		
5.2.3.2 Activities		
5.3 Streamlining Data Review	▪ None	NA
5.3.1 Data Review Steps To Be Streamlined		
5.3.2 Criteria for Streamlining Data Review		
5.3.3 Amounts and Types of Data Appropriate for Streamlining		

QAPP Worksheet #3
Distribution List

QAPP RECIPIENTS	TITLE	ORGANIZATION	TELEPHONE NUMBER	E-MAIL ADDRESS	DOCUMENT CONTROL NUMBER
Michael Berkoff (2 copies)	Remedial Project Manager 12th Street Landfill	U.S. EPA, Region 5	312.353.8983	berkoff.michael@epa.gov	56394 (3)-001
Sam Chummar (2 copies)	Remedial Project Manager Plainwell Mill	U.S. EPA, Region 5	312.886.1434	chummar.sam@epamail.epa.gov	56394 (3)-001
Richard Gay	Environmental Manager	Weyerhaeuser	501.624.8554	richard.gay@weyerhaeuser.com	56394 (3)-001
Martin Lebo	Senior Aquatic Scientist	Weyerhaeuser	252.633.7511	martin.lebo@weyerhaeuser.com	56394 (3)-001
Gregory Carli	Project Manager	CRA	905.682.0510	gcarli@craworld.com	56394 (3)-001
Emily Stahl	Project Coordinator (Plainwell Mill)	CRA	905.682.0510	estahl@craworld.com	56394 (3)-001
Jodie Dembowske	Project Coordinator (12th Street Landfill)	CRA	269.344.1230	jdembowske@craworld.com	56394 (3)-001
Paul Wiseman	QA Officer	CRA	734.453.5123	pwiseman@craworld.com	56394 (3)-001
Golnoush Bolourani	Field QA Officer	CRA	905.682.0510	gbolourani@craworld.com	56394 (3)-001
Dennis Catalano	Laboratory Manager	WATS	253.924.6242	dennis.catalano@weyerhaeuser.com	56394 (3)-001

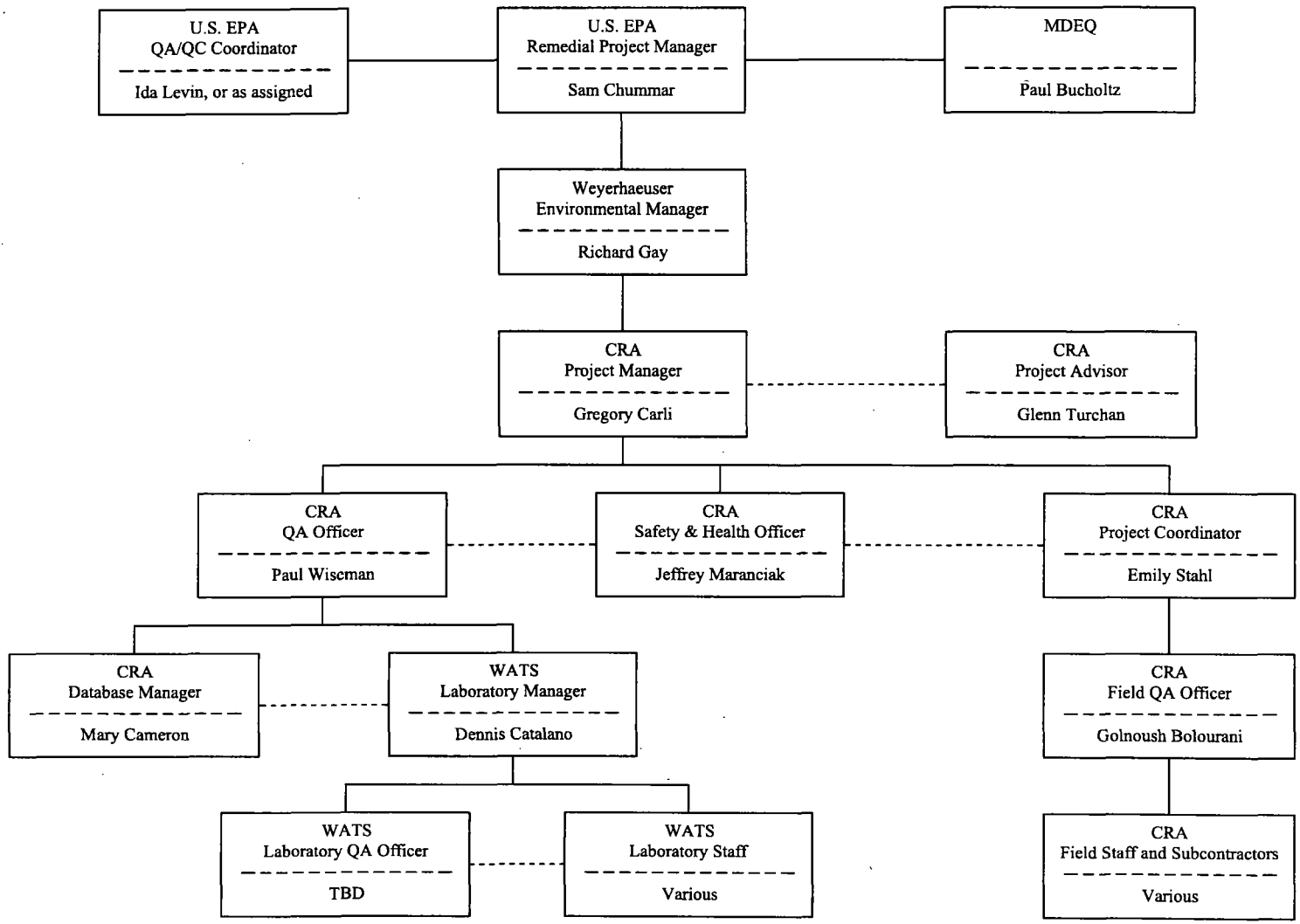
QAPP Worksheet #4-2
Project Personnel Sign-Off Sheet (WATS)

PROJECT PERSONNEL	TITLE	TELEPHONE NUMBER	SIGNATURE	DATE QAPP READ
Dennis Catalano	Laboratory Manager	253.924.6242		

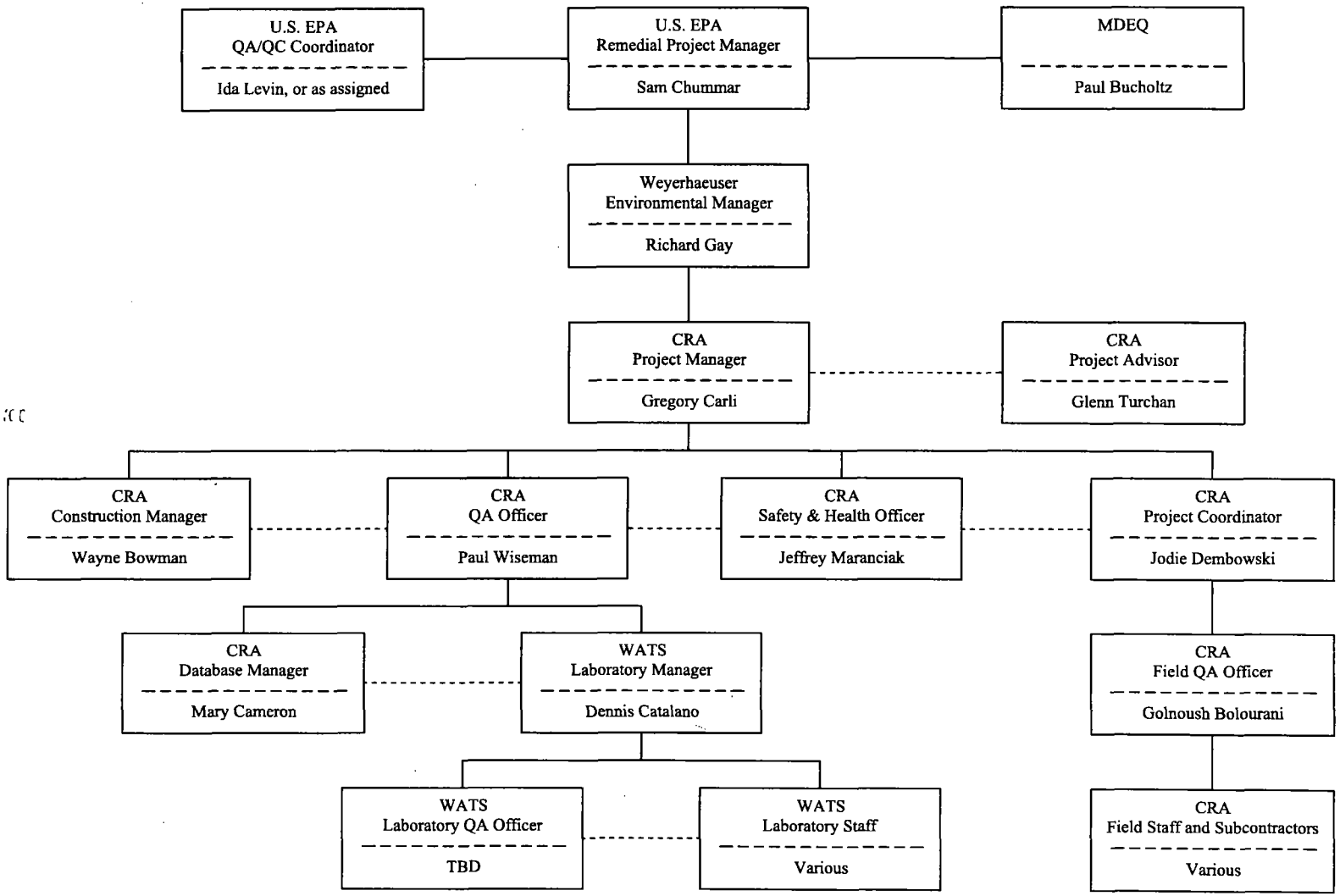
QAPP Worksheet #4-3
Project Personnel Sign-Off Sheet (CRA)

PROJECT PERSONNEL	TITLE	TELEPHONE NUMBER	SIGNATURE	DATE QAPP READ
Gregory Carli	Project Manager	905.682.0510		
Paul Wiseman	QA Officer	734.453.5123		
Golnoush Bolourani	Field QA Officer	905.682.0510		

QAPP Worksheet # 5-4
Project Organizational Chart
Plainwell Mill Phase II RI Work Plan



QAPP Worksheet # 5-5
Project Organizational Chart
12th Street Landfill Remedial Action Work Plan



QAPP Worksheet #6-4
Communication Pathways
Plainwell Mill Phase II RI Work Plan

COMMUNICATION DRIVERS	RESPONSIBLE ENTITY	NAME	TELEPHONE NUMBER	PROCEDURE (timing, pathways, etc.)
Phase II RI Work Plan- Former Plainwell, Inc Mill Property				
Serve as Point-of-Contact with U.S. EPA Remedial Project Manager (RPM)	Environmental Manager	Richard Gay Weyerhaeuser	501.624.8554	Richard Gay will provide project submittals to Michael Berkoff, U.S. EPA, in accordance with the schedule provided on Worksheet No. 16 of this QAPP.
Manage all project phases	Project Manager	Gregory Carli, CRA	905.682.0510	Gregory Carli will be the CRA liaison to the U.S. EPA for emergency response activities at the Plainwell Mill and 12th Street Landfill properties.
Coordination of project activities under supervision of Gregory Carli	Project Coordinator	Emily Stahl, CRA	905.682.0510	Emily Stahl will provide Gregory Carli with an update of project activities including data review and display, data evaluation and analysis, sampling plan preparation and supervision of implementation field sampling activities. Emily Stahl will report any QA/QC problems related to field measurements to the QA Officer (Paul Wiseman) by telephone or e-mail by the end of the same business day.
Provide assistance with Site Specific Health and Safety	Safety & Health Officer	Jeffery Maranciak, CRA	412.449.0812	Jeffery Maranciak will provide assistance to Project Coordinator and Field QA Officer (Golnoush Bolourani) with Site Specific Health and Safety Orientation to all CRA staff. Jeffery Maranciak will provide Gregory Carli with any problems related to filed health and safety concerns.

QAPP Worksheet #6-4
Communication Pathways
Plainwell Mill Phase II RI Work Plan

COMMUNICATION DRIVERS	RESPONSIBLE ENTITY	NAME	TELEPHONE NUMBER	PROCEDURE (timing, pathways, etc.)
Notify Gregory Carli, Emily Stahl, and the QA Officer of any QAPP changes in the field	Field QA Officer	Golnoush Bolourani, CRA	905.682.0510	Golnoush Bolourani will provide Gregory Carli and Emily Stahl with daily progress report on implementation of field activities and any changes to the QAPP made in the field by e-mail or fax within 2 business days. Golnoush Bolourani will also provide Gregory Carli and Emily Stahl with any QA/QC problems related to field measurements by telephone or e-mail by the end of the same business day.
Reporting lab data quality issues	Laboratory Manager	Dennis Catalano, WATS	253.924.6242	Dennis Catalano will notify the QA officer (Paul Wiseman) with any QA/QC issues within 2 business days.
Field and analytical corrective actions	QA Officer	Paul Wiseman, CRA	734.453.5123	Paul Wiseman will determine the need for corrective action for field and analytical issues, in conjunction with the Gregory Carli and Emily Stahl, or the Laboratory Manager, as appropriate.
Release of final analytical data	QA Officer	Paul Wiseman, CRA	734.453.5123	No final analytical data can be released until validation is complete and Paul Wiseman has approved the release.
QAPP amendments	QA Officer	Paul Wiseman, CRA	734.453.5123	Any major changes to the QAPP must be approved by Paul Wiseman, Gregory Carli, and the U.S. EPA before the changes can be implemented
Establish and maintenance of project database	Database Manager	Mary Cameron	734.453.5123	Mary Cameron will provide analytical data to Paul Wiseman and Rawa Fleisher

QAPP Worksheet #6-5
Communication Pathways
12th Street Landfill Remedial Action Work Plan

COMMUNICATION DRIVERS	RESPONSIBLE ENTITY	NAME	TELEPHONE NUMBER	PROCEDURE (timing, pathways, etc.)
Remedial Action (RA) – 12th Street Landfill				
Serve as Point-of-Contact with U.S. EPA Remedial Project Manager (RPM)	Environmental Manager	Richard Gay Weyerhaeuser Company	501.624.8554	Richard Gay will provide project submittals to Sam Chummar, U.S. EPA, in accordance with the schedule provided on Worksheet No. 16 of this QAPP.
Manage all project phases	Project Manager	Gregory Carli, CRA	905.682.0510	Gregory Carli will be the CRA liaison to the U.S. EPA for emergency response activities at the Plainwell Mill and 12th Street Landfill properties.
Coordination of project activities under supervision of Gregory Carli	Project Coordinator	Jodie Dembowske, CRA	412.449.0812	Jodie Dembowske will provide Gregory Carli with an update of project activities including data review and display, data evaluation and analysis, sampling plan preparation and supervision of implementation field sampling activities. Jodie Dembowske will report any QA/QC problems related to field measurements to the QA Officer (Paul Wiseman) by telephone or e-mail by the end of the same business day.
Provide assistance with construction and redevelopment	Construction Manager	Wayne Bauman, CRA	269.344.1230	Wayne Bauman will provide Gregory Carli with an update of construction activities, including related questions or problems, by telephone or e-mail at the end of each business day.
Provide assistance with Site Specific Health and Safety	Safety & Health Officer	Jeffery Maranciak, CRA	412.449.0812	Jeffery Maranciak will provide assistance to Project Coordinator and Field QA Officer (Golnoush Bolourani) with Site Specific Health and Safety Orientation to all CRA staff. Jeffery Maranciak will provide Gregory Carli with any problems related to filed health and safety concerns.

QAPP Worksheet #6-5
Communication Pathways
12th Street Landfill Remedial Action Work Plan

COMMUNICATION DRIVERS	RESPONSIBLE ENTITY	NAME	TELEPHONE NUMBER	PROCEDURE (timing, pathways, etc.)
Notify Gregory Carli, Jodie Dembowske, and the QA Officer of any QAPP changes in the field	Field QA Officer	Golnoush Bolourani, CRA	905.682.0510	Golnoush Bolourani will provide Gregory Carli and Jodie Dembowske with daily progress report on implementation of field activities and any changes to the QAPP made in the field by e-mail or fax within 2 business days. Golnoush Bolourani will also provide Gregory Carli and Jodie Dembowske with any QA/QC problems related to field measurements by telephone or e-mail by the end of the same business day.
Reporting lab data quality issues	Laboratory Manager	Dennis Catalano, WATS	253.924.6242	Dennis Catalano will notify the QA Officer (Paul Wiseman) with any QA/QC issues within 2 business days.
Field and analytical corrective actions	QA Officer	Paul Wiseman, CRA	734.453.5123	Paul Wiseman will determine the need for corrective action for field and analytical issues, in conjunction with the Gregory Carli and Jodie Dembowske, or the Laboratory Manager, as appropriate.
Release of final analytical data	QA Officer	Paul Wiseman, CRA	734.453.5123	No final analytical data can be released until validation is complete and Paul Wiseman has approved the release.
QAPP amendments	QA Officer	Paul Wiseman, CRA	734.453.5123	Any major changes to the QAPP must be approved by Paul Wiseman, Gregory Carli, and the U.S. EPA before the changes can be implemented
Development and maintenance of database	Database Manager	Mary Cameron	734.453.5123	Mary Cameron will provide analytical data to Paul Wiseman and Rawa Fleisher

QAPP Worksheet #7
Personnel Responsibilities and Qualifications

NAME	PROJECT ROLE	ORGANIZATIONAL AFFILIATION	EDUCATION AND EXPERIENCE QUALIFICATIONS
Michael Berkoff Sam Chummar	Remedial Project Manager - 12th Street Landfill Remedial Project Manager - Plainwell Mill	U.S. EPA, Region 5	Designated as the U.S. EPA's Project Coordinators
Richard Gay	Environmental Manager	Weyerhaeuser	
Gregory Carli, P. E.	Project Manager	CRA	B.A.Sc. Civil Engineering, Water Resources Option, University of Waterloo, 1996 Over 13 years of experience
Glenn Turchan, P. E.	Project Director	CRA	B.A.Sc. Geological Engineering, University of Waterloo M.A.Sc. Civil Engineering, University of Waterloo Over 24 years of experience
Emily Stahl	Project Coordinator Plainwell Mill	CRA	B.Sc. Earth Surface Science, University of Guelph Over 5 years experience
Jodie Dembowske	Project Coordinator 12th Street Landfill	CRA	M.Sc. Hydrogeology, Western Michigan University, 1994 B.Sc. Geology, Western Michigan University, 1991 Over 16 years experience
Paul Wiseman	QA Officer	CRA	B.Sc. Chemistry and Biology, Northern Michigan University, 1980 Over 29 years experience
Wayne Bauman	Construction Manager – 12th Street Landfill	CRA	B.A.Sc. Industrial Engineering, Minor Mathematics, Western Michigan University, 1986 Over 23 years experience
Jeffrey Maranciak	Safety & Health Officer	CRA	B.S. Safety & Environmental Management, Slippery Rock University, 1997 Over 12 years experience
Dennis Catalano	Laboratory Manager	WATS	B.S. Biology with chemistry minor, University of Dayton, 1977 30 years of experience

QAPP Worksheet #7
Personnel Responsibilities and Qualifications

NAME	PROJECT ROLE	ORGANIZATIONAL AFFILIATION	EDUCATION AND EXPERIENCE QUALIFICATIONS
Golnoush Bolourani	Field QA Officer	CRA	B.A.Sc. Materials Science and Engineering, University of Toronto, 2004 M.A.Sc. Environmental Engineering, Concordia University, 2008 Over 3 years of experience
Mary Cameron	Database Manager	CRA	B.S. Microbiology, University of Michigan, 1984 Assoc. Computer Information Systems, Henry Ford Community College, Dearborn, Michigan, 2001 Over 18 years of experience

U. S. EPA

Remedial Project Manager

- Serve as the primary point-of-contact for the U.S. EPA.
- Review and approve project submittals.
- Coordinate with the Michigan DEQ and other regulatory agencies as needed.
- Monitor project activities.

QA/QC Coordinator

- Review and approve the QAPP.
- Review and approve relevant portions of submitted documents to ensure compliance with the QAPP.
- Coordinate audits, as necessary.

WEYERHAEUSER COMPANY

Environmental Manager

- Serve as the primary point-of-contact between Weyerhaeuser Company and the U.S. EPA.
- Coordinate communications between Weyerhaeuser, CRA, the U.S. EPA, and other parties.
- Review draft project deliverables prior to their submittal to the U.S. EPA.

CRA

Project Manager

- Serve as the primary point-of-contact for CRA.
- Communicate with Weyerhaeuser Company, the U.S. EPA, and other project stakeholders.
- Establish and communicate project milestones and schedules.
- Coordinate and review CRA work products.
- Direct CRA team members.
- Provide technical input during the planning, design, and implementation stages of the project.
- Review the technical aspects of CRA's submittals.
- Approval of Quality Assurance Project Plan (QAPP).
- Preparation & Review of QAPP

Project Director

- Provide overall quality assurance, including a review of CRA's performance on the project.
- Review project progress and CRA work products for compliance with project objectives and requirements.
- Provide input regarding Superfund procedures and compliance with the National Contingency Plan (NCP).

Project Coordinator

- Review existing data, project objectives, and regulatory guidance to assist in the development of project sampling protocols.
- Review and summarize the results of data collected during project implementation, and make preliminary recommendations to the CRA Project Manager regarding the results (*e.g.*, whether additional data collection or field modifications appear to be necessary).

Field QA Officer

- Coordinate environmental staff who will be measuring and recording field parameters, collecting samples, and documenting construction activities, to ensure compliance with this QAPP.
- Order sample bottles from the laboratory.
- Prepare reports pertaining to relevant field activities.
- Maintain field and laboratory files, including project documentation, sample logs, and calculations; and provide complete copies to the CRA Project Coordinator.
- Conduct field audits, as necessary.

Safety Health Officer

- Provide assistance to the Field QA Officer and on-Site staff with Site specific Health and Safety Orientation to all CRA staff and subcontractors, and monitoring site activities for compliance with the project Health and Safety Plan.

Construction Manager

- Coordinate and direct subcontractors and CRA personnel who are performing construction work (*e.g.*, site preparation, excavation).
- Assist Field QA Officer with Health and Safety Orientations for construction-related activities.
- Maintain field records related to construction activities, and provide complete copies to the CRA Project Manager.

QA Officer

- Serve as the primary point-of-contact with the laboratory.
- Coordinate field QA/QC procedures with the Project Coordinator (*e.g.*, calibrations for field analytical measurements, and field audits, as necessary), and review pertinent field records for compliance with this QAPP.
- Review laboratory QA/QC procedures and documentation, as provided in data deliverables.
- Review data for compliance with the Data Quality Objectives (DQOs) for the project.
- Coordinate data validation activities and QA/QC reports preparation.

Database Manager

- Establish and maintain a project database.
- Import electronic data deliverables (EDDs) provided by the laboratory into the project database.
- Perform a QA/QC check of imported data versus the hard copy data.
- Transcribe field and non-EDD laboratory data into the project database, as necessary.
- Tabulate data for end users.

ANALYTICAL LABORATORY

Laboratory Manager

- Serve as the primary point-of-contact for the laboratory.
- Oversee preparation of analytical reports.
- Verify that the laboratory meets the QA/QC standards specified in this QAPP.
- Supervise in-house chain-of-custody.
- Perform laboratory audits, in accordance with this QAPP.

QAPP Worksheet #8
Special Personnel Training Requirements

PROJECT FUNCTION	SPECIALIZED TRAINING - TITLE OR DESCRIPTION OF COURSE	TRAINING PROVIDER	TRAINING DATE	PERSONNEL/ GROUPS RECEIVING TRAINING	PERSONNEL TITLES/ ORGANIZATIONAL AFFILIATION	LOCATION OF TRAINING RECORDS/ CERTIFICATES
Field activities	40-hour HAZWOPER and 8-hour HAZWOPER refresher	Certified training professionals	8-hour refresher within previous year	Field personnel	CRA personnel	CRA project offices
Confined Space Entry	Confined space training and testing, if applicable	Certified training professionals	4-hour training	Field personnel	CRA personnel	CRA project offices
Analytical chemistry	No state laboratory certification program in Michigan[1]	N/A	N/A	N/A	Weyerhaeuser Analysis and Testing Services (WATS) Weyerhaeuser Company Mail Stop: WTC2F25 32901 Weyerhaeuser Way Federal Way, WA 98001 Dennis Catalano 253.924.6242	N/A

Footnote:
[1] WATS is certified by the State of Washington.

QAPP Worksheet #9-6
Project Scoping Session Participants Sheet (May/June 2009)

Project Name: Former Plainwell, Inc Mill Property

Projected Date(s) of Sampling: 2009 **Site Name:** Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site

CRA Project Managers: Gregory Carli **Location of Scoping Session:** Conference Call

Date of Sessions: May 20, 2009 Phase II RI Work Plan and June 17, 2009 Conference Call

Scoping Session Purpose: To discuss the Phase II RI Work Plan

NAME	TITLE	AFFILIATION	TELEPHONE NUMBER	E-MAIL ADDRESS	PROJECT ROLE
Sam Chummar	Remedial Project Manager	U.S. EPA Region 5	312.353.8983	chummar.sam@epa.gov	U.S. EPA Project Manager
Richard Gay	Environmental Manager	Weyerhaeuser	501.624.8554	richard.gay@weyerhaeuser.com	Weyerhaeuser Environmental Manager
Martin Lebo	Senior Aquatic Scientist	Weyerhaeuser	252.633.7511	martin.lebo@weyerhaeuser.com	Technical Assistance
Gregory Carli	Project Manager	CRA	905.682.0510	gcarli@craworld.com	CRA Project Manager
Emily Stahl	Project Coordinator	CRA.	905.682.0510	estahl@craworld.com	CRA Project Coordinator

QAPP Worksheet #9-6
Project Scoping Session Participants Sheet (May/June, 2009)

Comments/Decisions:

- Discussion and comment regarding the proposed analyte list.
- As applicable, Weyerhaeuser will identify potential scenarios under which field modifications (e.g., additional test pits, changes in location or methods) may be needed.

Action Items:

- Respond to Comments and submit the revised Work Plan – completed (05/20/2009)

Consensus Decisions:

- Characterization of material for offsite disposal will include a PID measurements.
- Characterization of material selected for disposal will be disposed of properly according to applicable state and federal regulations.
- Need to submit a full work plan for the Plainwell Mill RI/FS.

QAPP Worksheet #9-7
Project Scoping Session Participants Sheet (April-June, 2009)

Project Name: 12th Street Landfill

Projected Date(s) of Sampling: 2009/2010 **Site Name:** Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site

CRA Project Managers: Gregory Carli **Location of Scoping Session:** Conference Call

Date of Sessions: Conference Calls on April 17, 2009 and May 1, 2009

Scoping Session Purpose: To discuss the revisions to the Remedial Design

NAME	TITLE	AFFILIATION	TELEPHONE NUMBER	E-MAIL ADDRESS	PROJECT ROLE
Michael Berkoff	Remedial Project Manager	U.S. EPA Region 5	312.353.8983	chummar.sam@epa.gov	U.S. EPA Project Manager
Paul Bucholtz	Superfund Section - Specialized Sampling Unit - Project Manager	MDEQ	517.373.8174	bucholtp@michigan.gov	MDEQ Project Manager
Richard Gay	Environmental Manager	Weyerhaeuser	501.624.8554	richard.gay@weyerhaeuser.com	Weyerhaeuser Environmental Manager
Martin Lebo	Senior Aquatic Scientist	Weyerhaeuser	252.633.7511	martin.lebo@weyerhaeuser.com	Technical Assistance
Gregory Carli	Project Manager	CRA	905.682.0510	gcarli@craworld.com	CRA Project Manager
Jodie Dembowske	Project Coordinator	CRA	269.344.1230	jdembowske@craworld.com	CRA Project Coordinator

QAPP Worksheet #9-7
Project Scoping Session Participants Sheet (April-June, 2009)

Comments/Decisions:

- Concept of design changes, mainly landfill slope from 4:1 to 3:1.
- Does not impact post excavation sampling approach.

Action Items:

- Prepare Pre-Final Design Report Addendum No. 1 in three Submittals

Consensus Decisions:

- Concept of design changes agreeable to all partners, pending review of design submittals.

QAPP Worksheet #10-5
Problem Definition - DQOs
Plainwell Mill Phase II RI Work Plan

Step 1: State the problem.

As approved by U.S. EPA on August 6, 2008, the Remedial Investigation is being implemented in a phased approach. The Phase II RI Work Plan is in accordance with Statement of Work (SOW) for the Remedial Investigation and Feasibility Study and the terms of the Consent Decree for the Design and Implementation of Certain Response Actions at Operable Unit #4 and the Plainwell, Inc Mill Property of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site (Consent Decree), which became effective February 22, 2005.

From early 1950s to 1970s carbonless papers were recycled at the mill, a process that released a waste stream containing PCBs to Kalamazoo River. In addition until the early 1950s, wastewater from paper making operations were discharged directly to the Kalamazoo River. By the mid-1950s, wastewater treatment facilities were in place at the Site and in late 1960s the treatment facilities improved. In early 1980s, the treatment facilities were improved by construction of a new wastewater treatment facility, consisting of a new primary clarifier, a mechanical dewatering system, a new secondary clarifier, and an activated sludge treatment system.

This Phase II RI Work Plan includes field sampling and analysis activities, consisting of a soil and supplemental groundwater investigation, which are required to complete the RI pursuant to the SOW, and constitutes the final phase of the RI.

Step 2: Identify the goal of the study.

The key goals of the data collection activities for the Phase II RI Work Plan as follows:

- Perform a supplemental groundwater investigation to further evaluate the nature and extent of impacts to groundwater and their potential sources;
- Further assess shallow, site-specific hydrogeologic characteristics and interconnections with the Kalamazoo River; and
- Perform soil investigations in the former wastewater sludge and dewatering lagoon and aeration basin area, the area of the mill buildings, and the north central portion of the mill, to adequately characterize the nature and extent of impacts to soil in the unsaturated zone that may have occurred due to historical operations of the mill.

Step 3: Identify information inputs.

Decision inputs for Phase II RI Work Plan are to determine the nature and extent of the contamination to assess risk and support development and evaluation of remedial alternatives, to evaluate potential risk, and to develop and evaluate remedial alternatives.

Step 4: Define the boundaries of the sampling.

The area considered as part of this action includes the Plainwell, Inc Mill Property located at 200 Allegan Street, Plainwell, Michigan (see Figure 2-4).

QAPP Worksheet #10-5
Problem Definition - DQOs
Plainwell Mill Phase II RI Work Plan

Step 5: Develop the analytical approach.

- Surface water samples will be analyzed for low level mercury, methyl mercury, and hardness.
- Soil samples will be analyzed for Target Compound List (TCL) VOCs. TCL SVOCs, PCBs, Target Analyte List (TAL) metals. Synthetic Precipitation Leaching Procedure (SPLP) metals, and general chemistry; and
- Groundwater from monitoring locations will be analyzed for TCL VOCs, TAL SVOCs, PCBs, and TAL inorganics. In addition two surface water samples will be collected and analyzed for low level mercury, methyl mercury, and hardness.

Step 6: Specify performance or acceptance criteria.

The acceptance criteria for the Phase II RI Work Plan activities are having collected sufficient information to meet the study objectives described under Step 2 above and sufficient information to proceed with the investigation. If these criteria are not met, additional data will be collected in a similar manner to meet these objectives.

Step 7: Develop the plan for obtaining the data.

The overall QA objective is to develop and implement procedures for field sampling that will provide results to support the evaluation of site data consistent with Michigan Part 201 Generic Residential Cleanup Criteria (GRCC) requirements. In general soil and groundwater sampling will be performed to provide representative adequate number of samples. Specific procedures for sampling, chain-of-custody, instrument calibration, analysis, reporting, and internal quality control are described in other worksheets of this QAPP.

QAPP Worksheet #10-6
Problem Definition - DQOs
12th Street Landfill Remedial Action Work Plan

Step 1: State the problem.

Operable Unit #4 (OU-4) of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site (Kalamazoo River Superfund Site) consists of the former 12th Street Landfill and the four areas outside the landfill where PCB-contaminated residual material has been observed. The 6.5 acre landfill is situated on an approximately 24-acre property with about 17 acres of wetlands. The additional portions of OU-4 that are located outside the landfill property include the woodland area owned by the State of Michigan (State) under the management of the Michigan Department of Natural Resources (MDNR), the asphalt plant operation adjacent to the landfill, and the former powerhouse discharge channel. A Record of Decision (ROD) for OU-4 was issued on September 28, 2001.

The scope of the RA for the 12th Street Landfill includes excavation of paper residuals present outside the footprint of the landfill (on adjacent properties), landfill grading, the construction of a landfill cover and erosion protection measures, and surface water management, landfill gas management, construction of access road, abandonment of existing groundwater monitoring wells, installation of groundwater monitoring wells, and various environmental monitoring activities.

Step 2: Identify the goal of the study.

The key goals of the activities for the RA Work Plan investigations are as follows:

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

- Confirmation of removal of paper residuals from the wetland north of landfill in accordance with the RA activities required by the ROD.

Asphalt Plant Property

- Confirmation of removal of paper residuals from the asphalt plant property in accordance with the RA activities required by the ROD.

MDNR Properties

- Confirmation of removal of paper residuals from the MDNR property in accordance with the RA activities required by the ROD.

Landfill Grading

- To implement an effective grading plan to prevent or minimize potential off-site damages; and
- To construct a final cover over the regarded landfill sideslopes and top portion of the landfill to meet the ROD requirements.

Landfill Gas Management

- To collect readily accessible information about the subsurface landfill gas conditions at the 12th Street Landfill that may be useful in designing a passive gas venting system for the landfill.

QAPP Worksheet #10-6
Problem Definition - DQOs
12th Street Landfill Remedial Action Work Plan

Step 3: Identify information inputs.

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

- Information inputs will include visual observations of extent of paper residuals base on color and consistency in accordance the ROD.

Asphalt Plant Property

- Information inputs will include visual observations of extent of paper residuals base on color and consistency in accordance the ROD; and
- Collection of verification sampling.

MDNR Properties

- Information inputs will include visual observations of extent of paper residuals base on color and consistency in accordance the ROD; and
- Collection of verification sampling.

Grading Design

- Information inputs will include global slope stability modeling to access the potential effect of the moisture and shear strength to meet requirements of State of Michigan solid waste management regulations (Part 115).

Landfill Gas Management

The information that is collected for determining the extent of paper residuals beyond the landfill footprint and for the grading design will be supplemented with similar visual information recorded during previous investigations at the 12th Street Landfill site.

The area considered as part of this action includes the Plainwell, Inc Mill Property located at 200 Allegan Street, Plainwell, Michigan (see Figure 2-4).

Step 5: Develop the analytical approach.

- Soil samples will be analyzed for TCL VOCs, TCL SVOCs, PCBs, TAL metals, SPLP metals, and general chemistry; and
- Groundwater from monitoring locations will be analyzed for TCL VOCs, TAL SVOCs, PCBs, and TAL inorganics. In addition two surface water samples will be collected and analyzed for low level mercury, methyl mercury, and hardness.

Step 6: Specify performance or acceptance criteria.

The acceptance criteria for the Phase II RI Work Plan activities are having collected sufficient information to meet the study objectives described under Step 2 above and sufficient information to proceed with the investigation. If these criteria are not met, additional data will be collected in a similar manner to meet these objectives.

Step 7: Develop the plan for obtaining the data.

The overall QA objective is to develop and implement procedures for field sampling that will provide results to support the evaluation of site data consistent with Michigan Part 201 Generic Residential Cleanup Criteria (GRCC) requirements. In general soil and groundwater sampling will be performed to provide representative adequate number of samples. Specific procedures for sampling, chain-of-custody, instrument calibration, analysis, reporting, and internal quality control are described in other worksheets of this QAPP.

QAPP Worksheet #11-5
Project Quality Objectives/Systematic Planning Process Statements
Plainwell Mill Phase II RI Work Plan

Who will use the data?

Weyerhaeuser, CRA, and the overseeing agencies including the U.S. EPA and the MDEQ will use the data.

What will the data be used for?

Surface Water Sampling:

The surface water data will be used to assess the compliance with applicable MDEQ Part 201 Criteria to determine the next steps.

Soil Sampling Activities:

The soil data will be used to assess the compliance with applicable MDEQ Part 201 Criteria to further characterize the soil quality at the mill.

Groundwater Monitoring:

The groundwater data will be used to assess the compliance with applicable MDEQ Part 201 Criteria to determine the next steps of investigations and characterize the groundwater flow direction.

What types of data are needed (target analytes, analytical groups, field-screening, on-site analytical or off-site laboratory techniques, sampling techniques)?

Sampling and analytical protocols are defined later in this document.

Surface Water Sampling:

Surface water samples will be analyzed for low level mercury, methyl mercury, and hardness.

Soil Sampling Activities:

Soil samples collected will be analyzed for TCL VOCs, TCL SVOCs, PCBs, TAL metals, SPLP metals, and general chemistry.

Groundwater Monitoring:

Groundwater samples collected will be analyzed for TCL VOCs, TAL SVOCs, PCBs, and TAL inorganics.

QAPP Worksheet #11-5
Project Quality Objectives/Systematic Planning Process Statements
Plainwell Mill Phase II RI Work Plan

How "good" do the data need to be in order to support the environmental decision?

Field parameter data must be collected with a meter that has a precision of at least ±0.01 pH unit, ±0.001 milliSiemen per centimeter (mS/cm) for conductivity, ±0.1 degree Celsius (C) for temperature, ±0.1 millivolts (mV) for dissolved oxygen, ±0.1 nephelometric turbidity units (NTUs) for turbidity; all data should be collected with a similar meter, calibrated per the manufacturer's requirements.

Surface Water Sampling:

To meet the objectives, representative surface water will be collected based on the hydrology and morphometrics at two locations at the millrace and Kalamazoo River to confirm the surface water quality. Samples collected for mercury will be analyzed for low level mercury, methyl mercury, and hardness in accordance with the performance standards of EPA Method.

Soil Sampling Activities:

Soil samples collected will be analyzed for TCL VOCs, TCL SVOCs, PCBs, TAL metals, SPLP metals, and general chemistry in accordance with the performance standards of EPA Methods.

Groundwater Monitoring:

Groundwater samples collected will be analyzed for TCL VOCs, TAL SVOCs, PCBs, and TAL inorganics in accordance with the performance standards of EPA Methods.

How much data are needed (number of samples for each analytical group, matrix, and concentration)?

Surface Water Sampling:

A minimum of two surface water samples will be collected to characterize the surface water quality at the millrace and Kalamazoo River.

Soil Sampling Activities:

Approximately 70 soil samples at various depths/locations will be collected to characterize the soil at the mill.

Groundwater Monitoring:

A minimum of 20 groundwater samples will be collected from existing and new monitoring well locations to further characterize the groundwater beneath the mill.

QAPP Worksheet #11-5
Project Quality Objectives/Systematic Planning Process Statements
Plainwell Mill Phase II RI Work Plan

Where, when, and how should the data be collected/generated?

Surface Water Quality Monitoring:

Field parameters will be taken prior sample collection. Samples will be collected at two locations: southeastern of the mill from the millrace and northeastern portion of the mill from Kalamazoo River. Samples will be collected according to the Phase II RI Work Plan schedule provided to U.S. EPA. The samples will be collected from either a boat or a shore-mounted semipermanent pier.

Soil Sampling Activities:

Soil samples will be collected at various locations according to Phase II RI Work Plan at various locations/depths. Soil samples will be collected according to the Phase II RI Work Plan schedule provided to U.S. EPA. Specific sampling methods will depend upon the depth soil sample is collected from. At each location a foot soil core will be collected and examined in the field for visual and/or olfactory evidence of impact. Additionally, soil cores will be screened across their entire length with a photoionization detector (PID) to determine the presence of undifferentiated volatile organic vapors. Evidence of visual, olfactory, or PID impacts will be recorded along with a description of the soil, in accordance with the Universal Soil Classification System (USCS).

Groundwater Monitoring:

Site-wide groundwater sampling will be conducted at the existing and new monitoring locations across the mill. Groundwater samples will be collected according to the Phase II RI Work Plan schedule provided to U.S. EPA. Monitoring wells will be purged using low flow sampling techniques to minimize drawdown and sediment agitation. Well purging will continue until three consecutive and consistent readings of the stabilization parameters (i.e., pH, temperature, conductivity, turbidity, oxygen reduction potential, and dissolved oxygen) are obtained.

Who will collect and generate the data?

CRA field personnel will collect the samples, the laboratory (WATS) will analyze the samples and issue data reports; and CRA QA Officer will coordinate data validation will release the data.

How will the data be reported?

Field parameters will be available from surface water quality monitoring and groundwater monitoring immediately after completion of field activities. Soil sampling data will be reported by the laboratory upon availability and validated data will be presented in the final summary report. Groundwater monitoring data will be reported by the laboratory upon availability and validated data will be presented in the final summary report.

How will the data be archived?

Validated data will be archived in an appropriate database to ensure that information is readily available, searchable, and compatible with a GIS system.

QAPP Worksheet #11-6
Project Quality Objectives/Systematic Planning Process Statements
12th Street Landfill Remedial Action Work Plan

Who will use the data?

Weyerhaeuser. CRA and the overseeing agencies including the U.S. EPA and the MDEQ will use the data.

What will the data be used for?

The data will be used for the following purposes:

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

- Confirmation of removal of paper residuals from the wetland north of landfill in accordance with the RA activities required by the ROD.

Asphalt Plant Property

- Confirmation and documentation of completion of the excavation activities at the asphalt plant property in accordance with the RA activities required by the ROD.

MDNR Properties

- Confirmation and documentation of completion of the excavation activities at the MDNR property in accordance with the RA activities required by the ROD.

What types of data are needed (target analytes, analytical groups, field-screening, on-site analytical or off-site laboratory techniques, sampling techniques)?

The data will be used for the following purposes:

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

- Field-screening will rely on the presence of visible residuals. The extent of excavation will be determined based on the visual confirmation and no soil sample will be collected.

Asphalt Plant Property

- The data will be used to confirm the extent of excavation. Field-screening will rely on the presence of visible residuals. Confirmatory soil sampling will be assessed by sampling for TCL VOCs and total PCBs using off-site analytical testing in a quick-turn analysis (i.e., 24-hours).

MDNR Properties

- The data will be used to confirm the extent of excavation. Confirmatory soil sampling will be assessed by sampling for total PCBs using off-site analytical testing in a quick-turn analysis (i.e., 24-hours).

Landfill Grading

- Completion of sampling is through global slope stability modeling.

Landfill Gas Management

- A modified Tier 3 testing program will (based on the U.S. EPA's Method 2E) will be implemented to obtain site-specific information regarding potential landfill gas generation and gas quality.

QAPP Worksheet #11-6
Project Quality Objectives/Systematic Planning Process Statements
12th Street Landfill Remedial Action Work Plan

How "good" do the data need to be in order to support the environmental decision?

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

- The extent of excavation will be determined based on the visual confirmation on-site and no verification soil sample will be collected.

Asphalt Plant Property

- The soil will be analyzed for TCL VOCs and total PCBs in accordance with the performance standards of EPA Methods

MDNR Properties

- The soil samples will be analyzed for total PCBs in accordance with the performance in accordance with the performance standards of EPA Methods.

How much data are needed (number of samples for each analytical group, matrix, and concentration)?

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

- The extent of excavation will be determined based on the visual confirmation on-site and no verification soil sample will be collected.

Asphalt Plant Property

- Approximately 13 verification soil samples will be collected. The actual number of samples to be collected on each will be determined following the exaction activities and will be adjusted to meet the MDEQ's Sampling Strategies and Statistic Training Material Part 201 Cleanup Criteria (S3TM)

MDNR Properties

- Approximately nine verification soil samples will be collected. The actual number of samples to be collected on each will be determined following the exaction activities and will be adjusted to meet the MDEQ's S3TM guidance.

Where, when, and how should the data be collected/generated?

Removal of Paper Residuals Beyond Landfill Footprint

Wetland

- The extent of excavation will be determined based on the visual confirmation on-site and no verification soil sample will be collected.

Asphalt Plant Property

- The soil samples will be collected from the base of the excavated and surface area of the sidewalls of the excavation from the top 6 inches of native soil below the surface of the exaction base and the sidewalls using a stainless-steel trowel and standard soil sampling and decontamination procedure. The excavation and soil sampling activities will be performed according to the RA Work Plan schedule provided to U. S. EPA.

MDNR Properties

- The soil samples will be collected from the base of the excavated and surface area of the sidewalls of the excavation from the top 6 inches of native soil below the surface of the exaction base and the sidewalls using a stainless-steel trowel and standard soil sampling and decontamination procedure. The excavation and soil sampling activities will be performed according to the RA Work Plan schedule provided to U. S. EPA.

Who will collect and generate the data?

CRA field personnel will collect the samples and generate the data, the laboratory (WATS) will analyze the collected field samples and issue data reports; and CRA QA Officer will coordinate data validation and release the analytical data.

QAPP Worksheet #11-6
Project Quality Objectives/Systematic Planning Process Statements
12th Street Landfill Remedial Action Work Plan

How will the data be reported? Soil sampling data will be reported by the laboratory upon availability in a quick-turn analysis (i.e., 24 to 72-hours) and validated data will be presented to determine the extent of the excavation.
How will the data be archived? Validated data will be archived in an appropriate database to ensure that information is readily available, searchable, and compatible with a GIS system.

QAPP Worksheet #12-1
Measurement Performance Criteria (PCBs - Surface Water)

Matrix: Aqueous
Analytical Group: PCBs
Concentration Level: All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-16	W-1	Precision - Overall	Relative percent difference (RPD) < 50%	Field duplicate	S&A
		Accuracy/Bias	% Recovery (%R) laboratory-generated limits[3]	Surrogate	A
		Accuracy/Bias Contamination	< Reporting limit (RL)	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R laboratory-generated limits[*]	Laboratory control sample (LCS)	A
		Accuracy/Bias and Precision	Retention times, see analytical SOP	Retention time windows	A
		Accuracy/Bias	%R, same as LCS[*]	Matrix spike (MS)[3]	A
		Accuracy/Bias	%R, same as LCS[*]	Matrix spike duplicate (MSD) or laboratory control sample duplicate (LCSD)[3]	A
		Precision	RPD <20%	MS/MSD or LCS/LCSD[3]	A

QAPP Worksheet #12-1
Measurement Performance Criteria (PCBs - Surface Water)

Footnotes:
(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.
(2) Reference number from QAPP Worksheet #23.
(3) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.
(*) See Attachments 1-1 and 1-2.
RPD = relative percent difference.

QAPP Worksheet #12-2
Measurement Performance Criteria (Wet Chemistry - Surface Water)

Matrix: Water
Analytical Group: Wet chemistry
Concentration Level: All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-16	W-2, W-3, W-5, W-26	Precision - Overall	RPD < 50%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, calibration, preparation)	S&A
		Accuracy/Bias	%R (90-110)	Continuing calibration verification	A
		Accuracy/Bias	%R (75-125)	MS[3]	A
		Accuracy/Bias	%R (75-125)	MSD[3]	A
		Precision	%R < 20%	MS/MSD[3]	A
		Accuracy/Bias	%R laboratory-generated limit[*]	LCS	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) MS and MSD not applicable for TSS

(*) See Attachment 1-1.

QAPP Worksheet #12-3
Measurement Performance Criteria (PCBs - Soil/Sediment)

Matrix: Soil/Sediment
Analytical Group:[1] PCBs
Concentration Level: All

SAMPLING PROCEDURE[2]	ANALYTICAL METHOD/SOP[3]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-4, F-5, F-6	W-4	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias	%R, laboratory-generated limits[*]	Surrogate	A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory-generated limits[*]	LCS	A
		Accuracy/Bias and Precision	Retention times, see analytical SOP	Retention time windows	A
		Accuracy/Bias	%R, same as LCS[*]	MS[3]	A
		Accuracy/Bias	%R, same as LCS[*]	MSD or LCSD[3]	A
		Precision	%RPD <35%	MS/MSD or LCS/LCSD[3]	A

QAPP Worksheet #12-3
Measurement Performance Criteria (PCBs - Soil/Sediment)

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1 and 1-2.

QAPP Worksheet #12-4
Measurement Performance Criteria (PCBs – Free Product)

Matrix: Free Product
Analytical Group: PCBs
Concentration Level: All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-8	S-1	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias	%R, laboratory-generated limits[*]	Surrogate	A
		Accuracy/Bias Contamination	< 2 x MDL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory-generated limits[*]	LCS	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	RPD <30%	MS/MSD or LCS/LCSD[4]	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1 and 1-2.

RPD = relative percent difference.

QAPP Worksheet #12-5
Measurement Performance Criteria (TAL Metals – Groundwater / SPLP Metals-Soil)

Matrix: Aqueous
Analytical Group: TAL Metals / SPLP Metals
Concentration Level: All (Except Low-Level Mercury)

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-8 F-11, F-5, F-6	W-14	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory-generated limits[(*)]	LCS	A
		Precision	sample > 5 x QL; RPD ≤ 20% sample ≤ 5 x QL: No limit	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory-generated limits[(*)]	MS[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[(*)]	MSD or LCSD[4]	A
		Precision	RPD <20%	MS/MSD or LCS/LCSD[4]	A
		Accuracy	%R > 80%	Interference check sample	A
		Accuracy	RPD ≤ 10%	Serial dilution	A

Footnotes:
(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.
(2) Reference number from QAPP Worksheet #23.
(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.
(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.
(*) See Attachments 1-1
RPD = relative percent difference.

QAPP Worksheet #12-6
Measurement Performance Criteria (TAL Metals-Soil)

Matrix: Soil
Analytical Group: TAL Metals
Concentration Level: All (Except Low-Level Mercury)

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-5, F-6	W-14	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory-generated limits[*]	LCS	A
		Precision	sample > 5 x QL; RPD ≤ 20% sample ≤ 5 x QL; No limit	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <40%	MS/MSD or LCS/LCSD[4]	A
		Accuracy	%R > 80%	Interference check sample	A
		Accuracy	RPD ≤ 10%	Serial dilution	A

Footnotes:
(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.
(2) Reference number from QAPP Worksheet #23.
(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.
(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.
(*) See Attachments 1-1
RPD = relative percent difference.

QAPP Worksheet #12-7
Measurement Performance Criteria (Cyanide - Groundwater)

Matrix: Aqueous
Analytical Group: Cyanide
Concentration Level: All, total

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-8, F-11	W-24	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory-generated limits	LCS	A
		Precision	%RPD <20%	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <20%	MS/MSD or LCS/LCSD[4]	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1.

RPD = relative percent difference.

QAPP Worksheet #12-8
Measurement Performance Criteria (Cyanide - Soil)

Matrix: Soil
Analytical Group: Cyanide
Concentration Level: All, total

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-5, F-6	W-25	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory-generated limits	LCS	A
		Precision	%RPD <20%	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <20%	MS/MSD or LCS/LCSD[4]	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1.

RPD = relative percent difference.

QAPP Worksheet #12-9
Measurement Performance Criteria (Low-Level Mercury and Methyl Mercury - Groundwater)

Matrix: Aqueous
Analytical Group: Mercury
Concentration Level: Low-Level

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-8, F-11	C-4, C-7	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory-generated limits[*]	LCS	A
		Precision	RPD	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <24%	MS/MSD or LCS/LCSD[4]	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1

RPD = relative percent difference.

QAPP Worksheet #12-10
Measurement Performance Criteria (SVOCs - Groundwater)

Matrix: Aqueous
Analytical Group: SVOCs
Concentration Level: All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-8, F-11	W-15	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, Laboratory-generated limits[*]	LCS	A
		Accuracy/Bias	%R, Laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, Laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <20%	MS/MSD or LCS/LCSD[4]	A
		Accuracy/Bias	%R, Laboratory-generated limits[*]	Surrogates	A
		Accuracy/Bias	+100%, -50% of ICAL	Internal standards	A
		Accuracy/Bias	Established mass limits	DFTPP Tuning	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1 and 1-2.

RPD = relative percent difference.

QAPP Worksheet #12-11
Measurement Performance Criteria (SVOCs - Soil)

Matrix: Soil
Analytical Group: SVOCs
Concentration Level: All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-5, F-6	W-15	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, Laboratory-generated limits[*]	LCS	A
		Accuracy/Bias	%R, Laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, Laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <40%	MS/MSD or LCS/LCSD[4]	A
		Accuracy/Bias	%R, Laboratory-generated limits[*]	Surrogates	A
		Accuracy/Bias	+100%, -50% of ICAL	Internal standards	A
		Accuracy/Bias	Established mass limits	DFTPP Tuning	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1 and 1-2.

RPD = relative percent difference.

QAPP Worksheet #12-12
Measurement Performance Criteria (VOCs - Groundwater)

Matrix: Aqueous
Analytical Group: VOCs
Concentration Level: All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-8, F-11	W-21	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory-generated limits[*]	LCS	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <20%	MS/MSD or LCS/LCSD[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	Surrogates	A
		Accuracy/Bias	+100%, -50% of ICAL	Internal standards	A
		Accuracy/Bias	Established mass limits	BFB Tuning	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1 and 1-2.

RPD = relative percent difference.

QAPP Worksheet #12-13
Measurement Performance Criteria (VOCs - Soil)

Matrix: Soil
Analytical Group: VOCs
Concentration Level: All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-5, F-6	C-5	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory-generated limits[*]	LCS	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <40%	MS/MSD or LCS/LCSD[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	Surrogates	A
		Accuracy/Bias	Established mass limits	BFB Tuning	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1 and 1-2.

RPD = relative percent difference.

QAPP Worksheet #12-14
Measurement Performance Criteria (DRO & GRO - Soil)

Matrix: Soil
Analytical Group: DRO, GRO
Concentration Level: All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-5, F-6	W-22 (DRO)	Precision-Overall	RPD < 100%	Field duplicate	S&A
	W-23 (GRO)	Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, Laboratory-generated limits	LCS	A
		Accuracy/Bias	%R, Laboratory-generated limits (50%-150%)	MS	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	%RPD <10%	MS/MSD or LCS/LCSD[4]	A
		Accuracy/Bias	%R, Laboratory-generated limits[*]	Surrogate	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1 and 1-2.

RPD = relative percent difference.

QAPP Worksheet #12-15
Measurement Performance Criteria (Wet Chemistry – Soil)

Matrix: Soil

Analytical Group: Wet chemistry

Concentration Level: All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-5, F-6	C-8, C-9 and C-10	Precision - Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, calibration, preparation)	S&A
		Accuracy/Bias	%R laboratory-generated limit[*]	Continuing calibration verification	A
		Accuracy/Bias	%R laboratory-generated limit[*]	MS[3]	A
		Accuracy/Bias	%R laboratory-generated limit[*]	MSD[3]	A
		Precision	%R laboratory-generated limit[*]	MS/MSD[3]	A
		Accuracy/Bias	%R laboratory-generated limit[*]	LCS	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) MS and MSD not applicable for Nitrogen compounds (Ammonia-N, Nitrate and Nitrite) and phosphorous.

(*) See Attachment 1-1.

QAPP Worksheet #12-16
Measurement Performance Criteria (Low-Level Mercury and Methyl Mercury – Surface Water)

Matrix: Aqueous
Analytical Group: Mercury
Concentration Level: Low-Level

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA[3]	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-16	C-4, C-7	Precision-Overall	RPD < 100%	Field duplicate	S&A
		Accuracy/Bias Contamination	< RL	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R, laboratory-generated limits[*]	LCS	A
		Precision	RPD, laboratory-generated limits	Laboratory duplicate	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MS[4]	A
		Accuracy/Bias	%R, laboratory-generated limits[*]	MSD or LCSD[4]	A
		Precision	%R, laboratory-generated limits[*]	MS/MSD or LCS/LCSD[4]	A

Footnotes:

(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.

(2) Reference number from QAPP Worksheet #23.

(3) Measurement performance criteria listed are current criteria at the time this document was created, but are subject to change as control limits are updated.

(4) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.

(*) See Attachments 1-1 and 1-2.

RPD = relative percent difference.

QAPP Worksheet #12-17
Measurement Performance Criteria (PCBs - Groundwater)

Matrix: Aqueous
Analytical Group: PCBs
Concentration Level: All

SAMPLING PROCEDURE[1]	ANALYTICAL METHOD/SOP[2]	DATA QUALITY INDICATORS (DQIs)	MEASUREMENT PERFORMANCE CRITERIA	QC SAMPLE AND/OR ACTIVITY USED TO ASSESS MEASUREMENT PERFORMANCE	QC SAMPLE ASSESSES ERROR FOR SAMPLING(S), ANALYTICAL(A), OR BOTH (S&A)
F-3, F-11, F-16	W-1	Precision - Overall	Relative percent difference (RPD) < 50%	Field duplicate	S&A
		Accuracy/Bias	% Recovery (%R) laboratory-generated limits[3]	Surrogate	A
		Accuracy/Bias Contamination	< Reporting limit (RL)	Blanks (field, equipment, method)	S&A
		Accuracy/Bias	%R laboratory-generated limits[*]	Laboratory control sample (LCS)	A
		Accuracy/Bias and Precision	Retention times, see analytical SOP	Retention time windows	A
		Accuracy/Bias	%R, same as LCS[*]	Matrix spike (MS)[3]	A
		Accuracy/Bias	%R, same as LCS[*]	Matrix spike duplicate (MSD) or laboratory control sample duplicate (LCSD)[3]	A
		Precision	RPD <20%	MS/MSD or LCS/LCSD[3]	A

QAPP Worksheet #12-17
Measurement Performance Criteria (PCBs - Groundwater)

Footnotes:
(1) Reference number from QAPP Worksheet #21. See the project-specific Field Sampling Plan for sampling procedures.
(2) Reference number from QAPP Worksheet #23.
(3) MS and MSD must be client-provided. LCS/LCSD performed when no MS/MSD is supplied.
(5) See Attachments 1-1 and 1-2.
RPD = relative percent difference.

QAPP Worksheet #13-1
Secondary Data Criteria and Limitations
12th Street Landfill RA Work Plan

SECONDARY DATA	DATA SOURCE (originating organization, report title, and date)	DATA GENERATOR(S) (originating organization, data types, data generation/ collection dates)	HOW DATA WILL BE USED	LIMITATIONS ON DATA USE
Soil and residuals sampling data	June and Sept. 1987 and January, 1989. MDNR and Mill Staff, 24 soil and residual samples outside berm. (Discussed in G&M, 1994a).	Plainwell Paper Co.; KRSG	Remedial design	U.S. EPA approval
Electromagnetic conductivity and magnetometer survey data	G&M, 1991. "12th Street Landfill Geophysical Investigation, Plainwell, Michigan." Letter Report by Geraghty and Miller, Inc. October 11, 1991.	Plainwell Paper Co.; KRSG	Remedial design	U.S. EPA approval
Soil and residuals sampling data	G&M, 1994a. "Test Pit Investigation, Technical Memorandum, 12th Street Landfill Operable Unit, Plainwell, Michigan, Allied Paper Inc./Portage Creek/Kalamazoo River Superfund Site." Geraghty and Miller, Inc. February 18, 1994.	Plainwell Paper Co.; KRSG	Remedial design	U.S. EPA approval
Sediment probing data; soil and residuals sampling data, groundwater sampling data	G&M, 1994b. Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund site Remedial Investigation/Feasibility Study, Technical Memorandum 8, 12th Street Landfill Operable Unit, Plainwell, Michigan. May 31, 1994.	Plainwell Paper Co.; KRSG	Site characterization	U.S. EPA approval[1]
Groundwater sampling data	G&M, 1996a. "Remedial Investigation Addendum I, 12th Street Landfill Operable Unit, Plainwell, Michigan, Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site." March 26, 1996.	Plainwell Paper Co.; KRSG	Remedial design	U.S. EPA approval
Summary of existing data; residuals sampling data	G&M, 1996b. "Remedial Investigation Report, 12th Street Landfill Operable Unit, Plainwell Michigan, Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site." Geraghty and Miller, Inc. December 20, 1996.	Plainwell Paper Co.; KRSG	Remedial design	U.S. EPA approval

QAPP Worksheet #13-1
Secondary Data Criteria and Limitations
12th Street Landfill RA Work Plan

SECONDARY DATA	DATA SOURCE (originating organization, report title, and date)	DATA GENERATOR(S) (originating organization, data types, data generation/ collection dates)	HOW DATA WILL BE USED	LIMITATIONS ON DATA USE
Geotechnical data	BBL, 2001a. "Geotechnical Sample Analytical Data, 12th Street Landfill Operable Unit." Transmittal Letter with Attachments. Blasland, Bouck & Lee, Inc. June 25, 2001.	KRSG	Remedial design	U.S. EPA approval
Sediment probing data	BBL, 2001b, as reported in final data summary report soil/sediment sampling results pre-design sampling. 12th Street Landfill, Operable Unit #4, Allied Paper, Inc./Portage Creek/Kalamazoo River Site, Plainwell, Michigan. July 2004.	KRSG	Site characterization	U.S. EPA approval[1]
Wetland delineation	CDM, 2002. "Michigan Department of Environmental Quality, Kalamazoo River and Portage Creek Wetland Delineation Study," Camp Dresser and McKee. January 2002.	MDEQ	Remedial design	U.S. EPA approval
Sediment probing data	U.S. EPA, 2004. Final data summary report soil/sediment sampling results pre-design sampling. 12th Street Landfill, Operable Unit #4, Allied Paper, Inc./Portage Creek/Kalamazoo River Site, Plainwell, Michigan. July 2004.	U.S. EPA	Site characterization	U.S. EPA approval[1]
Wastewater treatment system discharge, surface water, and residual data	RMT, Inc, 2007. Emergency Response Plan Design Report, 12th Street Landfill, Operable Unit #4, Allied Paper, Inc./Portage Creek/Kalamazoo River Site, Plainwell, Michigan. July 2007.	RMT	Site characterization	U.S. EPA approval
Summary of existing data including protective determination	U.S. EPA, 2007, First Five Year Review Report Final, 12th Street Landfill, Operable Unit #4, Allied Paper, Inc./Portage Creek/Kalamazoo River Site, Plainwell, Michigan, October 2007.	U.S. EPA	Site characterization	U.S. EPA approval

QAPP Worksheet #13-1
Secondary Data Criteria and Limitations
12th Street Landfill RA Work Plan

SECONDARY DATA	DATA SOURCE (originating organization, report title, and date)	DATA GENERATOR(S) (originating organization, data types, data generation/ collection dates)	HOW DATA WILL BE USED	LIMITATIONS ON DATA USE
Soil and paper residual sampling data	RMT, Inc, 2008. Remedial Design Work Plan report soil/residual sampling results pre-design sampling. 12th Street Landfill, Operable Unit #4, Allied Paper, Inc./Portage Creek/Kalamazoo River Site, Plainwell, Michigan. June 2008.	RMT	Remedial Design	U.S. EPA approval
Pre-final design investigation	RMT, Inc, 2008. Remedial Design Work Plan report soil/residual sampling results pre-design sampling. 12th Street Landfill, Operable Unit #4, Allied Paper, Inc./Portage Creek/Kalamazoo River Site, Plainwell, Michigan. June 2008.	RMT	Remedial Design	U.S. EPA approval

Footnote:

(1) Data and observations collected during the sediment excavation will take precedence.

QAPP Worksheet #13 -2
Secondary Data Criteria and Limitations
Plainwell Mill Phase II RI Work Plan

SECONDARY DATA	DATA SOURCE (originating organization, report title, and date)	DATA GENERATOR(S) (originating organization, data types, data generation/collection dates)	HOW DATA WILL BE USED	LIMITATIONS ON DATA USE
Sediment coring observations and survey results	RMT, July 2007. Visual Assessment of the Plainwell Mill Banks.	RMT July 2007	Site Characterization	U.S. EPA approval[1]
Prior investigations	BBL, 1996. Technical Memorandum 15: Mill Investigations	BBL 1996	Site Characterization	Data are historical and site conditions may have changed.
	ERM, 1997. Simpson Plainwell Paper Company Phase I environmental site assessment and Phase II investigation, Plainwell, Michigan	ERM 1997		
	Plainwell Paper, 1999 & 2000. Letter to Michigan Department of Environmental Quality.	Simpson Plainwell Oil spill clean-up samples 1999 & 2000		
	CDM, 2001. Plainwell Paper Gray Seam Investigation.	CDM October 2001		
	Weston, 2002. Removal Assessment Report for Allied Paper – Kalamazoo River Site, Otsego/Plainwell.	Weston July and August 2001		
	BBL, 2003. PCB Data for the Plainwell Impoundment River Bank Soil Samples.	BBL October 2003		
	FTCH, 2006. Phase II Environmental Site Assessment, Former Plainwell Paper Mill.	FTCH October 2006		
	RMT, 2008. Plainwell Mill Banks Emergency Action Documentation Report.	RMT January 2009.		
	RMT 2006, Draft RI/FS Work Plan Report, September 2006	RMT Document not finalized		

QAPP Worksheet #13 -2
Secondary Data Criteria and Limitations
Plainwell Mill Phase II RI Work Plan

SECONDARY DATA	DATA SOURCE (originating organization, report title, and date)	DATA GENERATOR(S) (originating organization, data types, data generation/collection dates)	HOW DATA WILL BE USED	LIMITATIONS ON DATA USE
	RMT 2009, Phase 1 Plainwell Mill RI/FS Work Plan: Summary of Test Pit Activities and Results for Plainwell Mill technical memorandum, January 2009	RMT January 2009		
	RMT 2009, Phase 1 Plainwell Mill RI/FS Work Plan: Initial Groundwater and Coal Tunnel Assessment Work Plan technical memorandum, February 2009	RMT February 2009		

Footnote:
(1) Data and observations collected during the sediment excavation will take precedence.

QAPP Worksheet #14
Summary of Project Tasks

SAMPLING AND ANALYSIS TASKS	
Emergency Response Activities in the Former Powerhouse Discharge Channel at the 12th Street Landfill (Operable Unit No. 4)	
Sampling tasks:	Sampling tasks will be performed as follows: Pre-excavation bathymetry measurements and sediment sampling to plan extent of sediment excavation (*i.e.*, analytical data for polychlorinated biphenyls (PCBs), visual characterization, and engineering data) Resuspension monitoring and control, including surface water sampling and field turbidity measurements Dewatering system discharge monitoring Post-excavation confirmation sampling for PCBs in channel sediment Global positioning system (GPS)–based survey of excavation limits and sampling locations Digital photographs
Analysis tasks:	Analytical samples will be processed, prepared, and analyzed, as follows: Resuspension monitoring and control (surface water) PCBs by WATS Dewatering system discharge monitoring (surface water) PCBs, total suspended solids (TSS), and phosphorus by WATS Post-excavation confirmation sampling (sediment) PCBs by WATS
Quality control tasks:	The samples will be collected and processed, and the laboratory waste will be disposed of as described in the laboratory SOPs (Attachment 1-5). QA samples will be collected as described in Worksheet #26.
Secondary data:	See Worksheets #13-1 and #13-2.

QAPP Worksheet #14
Summary of Project Tasks

SAMPLING AND ANALYSIS TASKS	
Predesign Investigations for the Remedial Design for the 12th Street Landfill (Operable Unit No. 4)	
Sampling tasks:	Field data collection activities during the predesign investigations will include: Visual information obtained by the advancement of test pits Visual information obtained by the advancement of Geoprobe® borings Gas concentrations (methane, carbon dioxide, and oxygen) measured in existing monitoring wells and in the Geoprobe® locations. Pressure measured in existing monitoring wells.
Analysis tasks:	No analytical data will be collected.
Quality control tasks:	No analytical data will be collected.
Secondary data:	See Worksheet #13-1.
Phase 2 of Addendum No. 1 – Test Pits & Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment	
Sampling tasks:	Sampling tasks will be performed as follows: **Phase 2 of Addendum No. 1** Approximately 15 test pits will be excavated along the banks of the Plainwell Mill buildings. Test pit excavation to determine extent of oil impacted soil and elevated concentrations of PCBs (*i.e.*, analytical data for polychlorinated biphenyls (PCBs) & total petroleum hydrocarbons, visual characterization, and engineering data) Additional soil samples will be collected from the test pits for RCRA metals, VOCs, and PAHs If free product is observed a sample will be collected for general characteristics Global positioning system (GPS)–based survey of excavation limits and sampling locations Digital photographs **Plainwell Mill RI/FS – Phase I Initial Groundwater Assessment** Approximately 12 groundwater wells and three staff gages will be installed. Collect groundwater samples for RCRA metals, VOCs, PAHs, and PCBs Collect water elevations from three surface water staff gages (Two in the Kalamazoo River and One in the Mill Race) Global positioning system (GPS)–based survey of excavation limits and sampling locations Digital photographs

QAPP Worksheet #14
Summary of Project Tasks

Analysis tasks:	Analytical samples will be processed, prepared, and analyzed, as follows: **Phase 2 of Addendum No. 1 - Test Pits Soil Samples** PCBs by WATS RCRA Metals by WATS PAHs by WATS VOCs by Columbia Analytical Services Free Product Characterization (Specific Gravity & Viscosity) – Summit Technologies, Inc. Total petroleum hydrocarbons (DRO/GRO) by WATS **Plainwell Mill RI/FS – Initial Groundwater Assessment (Groundwater Samples)** PCBs by WATS RCRA Metals by WATS Hg by Columbia Analytical Services PAHs by WATS VOCs by Columbia Analytical Services
Quality control tasks:	The samples will be collected and processed, and the laboratory waste will be disposed of as described in the laboratory SOPs (Attachment 1-5). QA samples will be collected as described in Worksheet #26.
Secondary data:	See Worksheets #13-1 and #13-2.
SAMPLING AND ANALYSIS TASKS	
Plainwell Mill Phase II Remedial Investigation Work Plan	
Sampling tasks:	Sampling tasks will be performed as follows: Advancement of soil boring and performing soil sampling as described in Worksheet# 18-5. Installation of monitoring wells at various location at the site. Performance of side-wide groundwater monitoring at existing and new monitoring locations. GPS–based survey of soil boring and groundwater monitoring locations. Collection of two surface water samples, one from millrace and one from Kalamazoo River. Digital photographs.

QAPP Worksheet #14
Summary of Project Tasks

Analysis tasks:	Analytical samples will be processed, prepared, and analyzed, as follows: Surface water sampling: Low level mercury, methyl mercury, and hardness subcontract by WATS to Columbia Analytical Services Soil sampling: TCL SVOCs, TAL Metals, SPLP Metals, and PCBs by WATS TCL VOCs and general chemistry subcontract by WATS to Columbia Analytical Services Groundwater monitoring: TCL VOCs, TCL SVOCs, PCBs, and TAL inorganics by WATS
Quality control tasks:	The samples will be collected and processed, and the laboratory waste will be disposed of as described in the laboratory SOPs (Attachment 1-5). QA samples will be collected as described in Worksheet #26.
Secondary data:	See Worksheets #13-1 and #13-2.
12th Street Landfill Remedial Action Work Plan	
Sampling tasks:	Sampling tasks will be performed as follows: Asphalt Plant Property Post- excavation soil sampling at the base of excavation and sidewalls of the excavated area. GPS–based survey of excavation limits and sampling locations. Digital photographs. MDNR Property Post- excavation soil sampling at the base of excavation and sidewalls of the excavated area GPS–based survey of excavation limits and sampling locations. Digital photographs.
Analysis tasks:	Analytical samples will be processed, prepared, and analyzed, as follows: Soil samples collected from Asphalt Plant Property: PCBs by WATS TCL VOCs subcontract by WATS to Columbia Analytical Services Soil sampling collected from MDNR Property: PCBs by WATS
Quality control tasks:	The samples will be collected and processed, and the laboratory waste will be disposed of as described in the laboratory SOPs (Attachment 1-5). QA samples will be collected as described in Worksheet #26.

QAPP Worksheet #14
Summary of Project Tasks

Secondary data:	See Worksheets #13-1 and #13-2.
DATA MANAGEMENT, DOCUMENTATION, RECORDS, AND AUDIT TASKS	
Data management tasks:	**Field data reduction** - Raw data from field measurements and sample collection activities will be recorded as specified in the FSP. If the data are to be used in the project reports, they will be reduced or summarized, and the method of reduction will be documented in the report. With the exception of the temperature correction for specific conductance, no calculation will be involved in field data reduction. Only direct-reading instrumentation will be employed in the field. The On-Site Coordinator or designee will proofread all forms and notebooks to determine if transcription errors have been made by the field crew. **Laboratory data reduction** - WATS (or subcontracted laboratory) will perform in-house analytical data reduction under the direction of the laboratory QA/QC Manager. The laboratory QA/QC Manager will be responsible for assessing data quality and advising of any data that were rated "preliminary" or "unacceptable" or of other notations that would caution the data user of possible unreliability. Data reduction, by the laboratory, will be conducted as follows: The analysts who produced the laboratory data will first conduct a systematic review (Level 1 Review). An experienced peer, supervisor, or designee will examine the data (the Level 2 Review) to ensure that the Level 1 review has been completed correctly and thoroughly. Following the Level 2 review, the data will be turned over to the Laboratory Project Manager for a third-level review. The Project Manager will review the data for completeness and attainment of quality control criteria as outlined in the U.S. EPA methods and for overall reasonableness. The Project Manager will verify the accuracy and completeness of the final reports. The Laboratory QA/QC Manager and the supervisor of the pertinent analytical section, in conjunction with the CRA QA Officer, will decide whether any sample reanalysis is required. Data reduction procedures are included in the U.S. EPA-approved methods and associated laboratory SOPs. **Field data reporting** - Field data reporting will consist of field logs and calibration and measurement records documenting site activities as described in the FSP and on the sample Chain-of-Custody (COC) Records.

QAPP Worksheet #14
Summary of Project Tasks

Data management tasks: ***(continued)***	**Laboratory data reporting** - The analytical laboratories will prepare and retain full analytical and QC documentation. Such retained documentation need not be on hard (paper) copy, but may be in other storage media (*e.g.*, computer diskette or magnetic tape). As needed, WATS will supply a hard copy of the retained information. WATS will provide the following information in each analytical data package submitted: Dated cover sheets, signed by the WATS project manager, listing a laboratory batch number; the analyses performed; the number of samples and respective matrices; the project name and number; narrative comments describing deviations from intended analytical strategy, and any problems encountered in analysis; a discussion of any laboratory quality control checks that failed to meet project criteria; and the signature of the laboratory QA/QC Manager Tabulated results of inorganic and organic compounds identified and quantified, including sample preparation and analysis dates, and cross-references of laboratory and field sample identification numbers Analytical results for QC sample spikes and sample duplicates; initial and continuing calibration verifications of standards and blanks; standard procedural blanks; laboratory control samples; and the data produced by ICP interference check samples, as appropriate for the specified analyses Tabulation of Method Detection Limits, as appropriate Raw data system printouts (or legible photocopies) identifying the date of analyses, the mass spectra tuning data, the name of the analyst, the parameters determined, the initial and continuing calibration, the calibration verification summary, the method blanks, the sample and any dilutions, sample duplicates and spikes, chromatograms, GC/MS spectra, computer printouts, internal standard area and RT summary, cleanup information, control samples, ICP outputs, and inter-element correction data WATS will provide the following information for the indicator parameters in each analytical data package submitted: Dated cover sheets listing a laboratory batch number; the analyses performed; the number of samples and respective matrices; project name and number; narrative comments describing deviations from intended analytical strategy, and problems encountered in analysis; discussion of any laboratory quality control checks that failed to meet project criteria; and the signature of the Laboratory QA Manager Copies of bench sheets that include summaries of initial calibration and continuing calibration check results Summary of QC sample analysis (spikes, duplicates, laboratory control samples, and blanks). A report will be prepared containing a QA/QC section summarizing the quality of the data. The QA report prepared by the CRA will address the assessment of data precision, accuracy, completeness, and comparability; the results of performance audits, if any; the results of system audits; any reported nonconformances; any significant QA/QC problems and recommended solutions; the results of corrective actions since the last report; and approved revisions to the QA/QC processes. The report will indicate whether the QA objectives were met and whether the data can be used for the intended purposes based on an evaluation of compliance with control limits, the results of audits, and compliance with the procedures specified in the QAPP and the FSP.

QAPP Worksheet #14
Summary of Project Tasks

Documentation and records:	Appropriate records will be maintained to provide adequate documentation of the entire data generation process, including field sampling and laboratory analysis. **Field documentation -** Field personnel will develop and retain comprehensive records of field activities, including field sampling, field analysis, and sample COC Record, to allow a reconstruction of field events and sample handing during data review and interpretation. **Laboratory project files -** WATS will maintain a file for pertinent project information, including COC Records; other custody documents (air bills, etc.); work orders; Sample Receipt Acknowledgment Forms, if any; instrument detection limit and control limit tabulations; all raw analytical data on bench sheets; laboratory data; and project communication records. Such retained documentation need not be on hard (paper) copy, but may be in other storage media (*e.g.*, computer diskette or magnetic tape). As needed, WATS will supply a hard copy of the retained information. **Laboratory notebooks -** Logbooks, bench sheets, instrument notebooks, and instrument printouts will be retained as part of the permanent laboratory record, including the associated quality controls. Each page in the laboratory logbooks and bench sheets will be signed and dated by the analyst, and errors will be crossed out in indelible ink. System printouts of raw inorganic and organic data will include dates of analyses; analyst's name; parameters determined; calibration curve; calibration verifications; method blanks; sample number and dilutions performed; and sample duplicates, spikes, and control samples. Internal laboratory QC sample results will be indicated on the analytical bench sheets and will include sample spikes, sample duplicates, initial and continuous calibration verification of standards and blanks, standard procedural blanks, laboratory control samples, ICP serial dilutions, and ICP interference check samples. **Computer and hard copy storage -** All electronic files and deliverables will be retained by the laboratory for no less than 5 years. Weyerhaeuser, or its designated representatives, will retain copies of the analytical data reports according to the requirements of the laboratory QA Manual. All field records will be kept in the central project file at the CRA offices at St. Catharines, Waterloo, or Kalamazoo; and records will be included in project reports, as appropriate or upon request by the U.S. EPA RPM. **Field data reporting -** Field data reporting will consist of field notebooks and logs, photographs, boring logs, calibration and measurement records, and COC documentation, including field quality control samples that will be collected to assess the quality of the analytical data and to evaluate sampling and analytical reproducibility. Field records will be reviewed by the CRA Project Manager for consistency with the planned activities, and any concerns will be discussed with the Field QA Officer. Field performance and field system audits will also be performed, as discussed below and in Worksheets #31 and 32. **Laboratory data reporting -** Analytical data for this project will be reported in both an electronic data deliverable (EDD) and an analytical data package. The EDD will be generated by WATS and will be used by CRA to facilitate loading the analytical data into the project database. The Laboratory QA/QC Manager will perform a final review of the report summaries and case narratives to determine if the report meets project requirements. The task of reporting laboratory data to the U.S. EPA will begin after the data review activity has been concluded. The validated analytical data will be provided to the U.S. EPA in accordance with the project schedule (Worksheet #16). In addition to the COC Record, WATS will prepare and provide a full "CLP-like" data package, including the following:

QAPP Worksheet #14
Summary of Project Tasks

Documentation and records: (*continued*)	**Case narrative** - date of issuance; laboratory analysis performed; any deviations from required analytical methods; laboratory sample lot numbers; numbers of samples and respective matrices; QC procedures used and references to the acceptance criteria; laboratory report table of contents; project name and number; condition of samples upon receipt; dates of extraction, preparation, and analysis; discussion of whether or not sample holding times were met; discussion of technical problems or other observations that may have created analytical difficulties; discussion of any laboratory QC checks that failed to meet project criteria; signature of the laboratory Project Manager, and copies of the COC Records **Chemistry data package** - run log, summary page indicating dates of analyses for samples and laboratory QC checks, cross-referencing of laboratory sample to project sample identification numbers, adequately described data qualifiers, sample preparation and analysis methods, sample results, matrix spike and matrix spike duplicate (MS/MSD) recoveries, laboratory control sample recoveries, method blank results, and surrogate recoveries Soil sample analytical data generated by the laboratory will be reported in micrograms per kilogram (µg/kg) on a dry-weight basis. Groundwater data will be reported in micrograms per liter (µg/L). Results between the laboratory Method Detection Limit (MDL) and the Quantitation Limit (QL) will be reported. Data retained in the project database may be converted to units other than those reported by the laboratories. Sample results will not be corrected for contamination found in laboratory blanks. However, sample results may be qualified as not detected based on laboratory, field, and/or trip blank contamination. WATS will provide the following information in each analytical data package submitted: Dated cover sheets, signed by the WATS Project Manager, listing a laboratory batch number; the analyses performed; the number of samples and the respective matrices; the project name and number; narrative comments describing deviations from intended analytical strategy, and problems encountered in analysis; a discussion of any laboratory quality control checks that failed to meet project criteria; and the signature of the laboratory QA/QC Manager Tabulated results of inorganic and organic compounds identified and quantified, including sample preparation and analysis dates, and cross-references of laboratory and field sample identification numbers Analytical results for QC sample spikes, sample duplicates, and blanks; initial and continuing calibration verifications of standards and blanks; standard procedural blanks; laboratory control samples; and the data produced by inductively coupled plasma (ICP) interference check samples, as appropriate for the specified analyses Tabulation of Method Detection Limits, as appropriate Raw data system printouts (or legible photocopies) identifying dates of analyses, mass spectra tuning data, name of analyst, parameters determined, initial and continuing calibration, calibration verification summary, method blanks, sample and any dilutions, sample duplicates and spikes, chromatograms, gas chromatograph/mass spectrophotometer (GC/MS) spectra, computer printouts, internal standard area and retention time (RT) summary, cleanup information, control sample results, ICP outputs, and inter-element correction data

QAPP Worksheet #14
Summary of Project Tasks

Assessment/Audit tasks:	Performance and system audits will be completed in the field and laboratory, as described below and in Worksheets #31 and 32. **Field audits** - The Project Manager will monitor day-to-day field performance through daily communications with the Project Coordinator and on-site field staff and the Construction Manager. In addition, field performance audits and field system audits will be performed, as follows: **Field performance audits** - Field performance audits will be conducted in order to confirm that the activities are being performed according to the established plans. The field performance audit(s) will be performed by the Senior Consultant QA Manager (or her designee), at a frequency that is appropriate for the field activities being performed. The audit(s) will include a discussion of the project progress with the Project Manager and/or the review of field reports, as appropriate. The Senior Consultant QA Manager will record and document any observations made during field system audits, and will discuss the audit and any recommended changes/deviations to the field procedures with the Project Manager. **Field system audits** - Field system audits will be performed by the CRA QA Officer, including a review of rinse and trip blank data to identify potential deficiencies in field sampling and decontamination procedures, and a comparison of the scheduled QA/QC activities described in this QAPP with the QA/QC procedures being performed on the project. Field system audits will be performed at a frequency appropriate for the field activities. The CRA QA Officer will record and document any observations made during field system audits, and will discuss the audit and any recommended changes/deviations to the field procedures with the Project Manager. **Laboratory audits** - Laboratory audits will be performed, as follows: **Internal audits** - The Laboratory QA/QC Manager (or his designee) will conduct internal laboratory audits periodically. This will include an overall evaluation of the performance of laboratory staff and a comparison of laboratory procedures with the laboratory QA Manual and SOPs. Results of the audits will be summarized and distributed to appropriate laboratory staff. **External audits** - The CRA QA Officer will review the laboratory QA Manual and applicable SOPs, and will discuss laboratory procedures with the Laboratory QA/QC Manager prior to the start of project sampling. The CRA QA Officer will record and document any observations made during the review. In addition, as a participant in state and federal certification programs, the laboratory is audited by representatives of the regulatory agency issuing certification. Audits include a review of sample handling and tracking documentation, analytical methodologies, analytical supportive documentation, and final reports. The audit findings are documented and submitted to the laboratory for corrective action, if necessary. **Corrective action** - Corrective actions are required when field or analytical data are not within the objectives specified in this QAPP, as follows:

QAPP Worksheet #14
Summary of Project Tasks

Assessment/Audit tasks: ***(continued)***	**Field measurement corrective action** - Corrective action in the field may be necessary when the sample network is changed (*i.e.*, more/fewer samples, sampling locations other than those specified in the FSP, etc.), or when sampling procedures and/or field analytical procedures require modification in response to unexpected conditions. Technical staff and project personnel will be responsible for reporting all suspected technical or QA nonconformances or deficiencies of any activity or issued document by reporting the situation to the CRA Project Coordinator or designee. The CRA Project Coordinator will assess the suspected problems in consultation with the CRA Project Manager or CRA QA Officer or designee, and will assist in making a decision based on the potential for the situation to impact the data quality. If it is determined that the situation warrants a reportable nonconformance requiring corrective action, the CRA Field QA Officer will initiate a nonconformance report. If appropriate, the CRA Field QA Officer will ensure that no additional work that is dependent on the nonconforming activity is performed until the corrective actions are completed. **Laboratory corrective action** - Corrective actions are required whenever an out-of-control event or potential out-of-control event is noted. Corrective actions may be necessary if any of the following occur: ▪ 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 the RPD between duplicates. ▪ There are unusual changes in detection limits. ▪ Deficiencies are detected by the Laboratory Manager during internal or external audits or from the results of performance evaluation samples. ▪ Inquiries concerning data quality are received. Corrective actions should be timely, and they should determine the root cause and evaluate any propagation of the error or problem. The investigative action taken is somewhat dependent on the analysis and the event. Corrective action in the laboratory may occur prior to, during, or after the initial analysis. Corrective action is under the supervision of the Laboratory Manager and Laboratory QA Officer. Following a consultation with laboratory scientists, technicians, and team leaders, it may be necessary for the Laboratory Manager to approve the implementation of the corrective action. Some conditions during or after analysis may automatically trigger corrective action or optional procedures. These conditions may include dilution of samples, additional sample extract cleanup, and automatic reinjection/reanalysis when certain quality control criteria are not met, etc. WATS' corrective action procedures are documented in Laboratory SOPs specifying corrective action to be taken when an analytical error is discovered or the analytical system is found to be out of control.

QAPP Worksheet #14
Summary of Project Tasks

Assessment/Audit tasks: ***(continued)***	Depending on the problem, the corrective action employed may be formal or informal. On-the-spot actions are used to correct minor problems, such as recalibration, retuning, or a minor repair (*e.g.*, replacement of a minor part) of a malfunctioning instrument or the correction of poor analytical technique being used. Corrective action procedures may be handled at the bench level by the analyst, who reviews the preparation or extraction procedure that was used for possible errors, and checks the instrument calibration, spike, and calibration mixes, and the instrument sensitivity. These occurrences are documented in the appropriate injection, run, or analysis logbooks. Similarly, routine instrument maintenance, malfunctions, and power failures are also documented in the appropriate instrument maintenance logbooks. If the problem persists or cannot be identified, the matter may be referred to the laboratory team leader, and/or QA/QC Manager for further investigation. Occurrence of the problem, the corrective action employed, and verification that the problem has been eliminated will be properly documented. The corrective action procedure will be discussed with the Laboratory Project Manager, and full documentation of the corrective action procedure, whether resolved or not, will be placed in the laboratory project file. Corrective actions specific to analytical methods are discussed in the operational-specific SOPs. The U.S. EPA RPM or the CRA QA Officer may request corrective action for any nonconformance identified by audits or data validation. **Corrective action during data validation and data assessment** - The need for corrective actions may be identified during data validation or data assessment. Potential types of corrective action may include resampling by the field team or reinjection/reanalysis of samples by the laboratory. Data validation corrective actions may include notification of the laboratory of incomplete or erroneous reports and a request for issuance of corrected versions. When the CRA QA Officer identifies a corrective action situation, the CRA Project Manager will approve the implementation of corrective action, including possible resampling. The CRA QA Officer will notify the laboratory of incomplete or erroneous reports and will request the issuance of corrected versions. All corrective actions will be documented. Final summary data tables will not be issued until all data have been validated and all corrections have been made. Corrective action may include the following: ▪ Reanalysis of samples, if holding time requirements permit ▪ Resampling and analysis ▪ Evaluation and amendment of sampling procedures ▪ Evaluation and amendment of analytical procedures ▪ Acceptance of data and acknowledgment of the level of uncertainty
Data Review tasks:	See Worksheets #36 and 37.

QAPP Worksheet #15-1
Reference Limits and Evaluation (Surface Water)

ANALYTE	CAS NUMBER	PROJECT ACTION LIMIT[1]	WATER (µg/L)[2]	
			LABORATORY MDL	LABORATORY RL
PCBs (U.S. EPA 608)[3]				
Aroclor - 1016	12674-11-2	--	0.10	0.2
Aroclor - 1221	11104-28-2	--	--	0.2
Aroclor - 1232	11141-16-5	--	--	0.2
Aroclor - 1242	53469-21-9	--	--	0.2
Aroclor - 1248	12672-29-6	--	--	0.2
Aroclor - 1254	11097-69-1	--	--	0.2
Aroclor - 1260	11096-82-5	--	0.10	0.2
Total PCBs	1336-36-3	0.2 µg/L	--	0.2
Metals				
Low Level Mercury	7439-97-6	--	0.08 ng/L	1 ng/L
Methyl Mercury	22967-92-6	--	0.05 ng/L	0.1 ng/L
Inorganics (Wet Chemistry)[4]				
TSS (U.S. EPA 160.2)	--	30-45 mg/L	--	5.0 mg/L[5]
Total phosphorus as P (U.S. EPA 365.2)	--	--	--	0.01 mg/L
Hardness (SM 2340B)-Calculation of Ca & Mg	14797-65-0	--	0.0033 mg/L	1.66 mg/L

Footnotes:

(1) Standards are consistent with the Multi-Area Quality Assurance Project Plan (Rev. 00) For the Kalamazoo River Study Group (Arcadis BBL, 2007b), which are from the MDEQ's Substantive Requirements Document for the Plainwell Dam Superfund Site, dated February 13, 2007. The TSS standards are on a monthly and daily basis, respectively.

(2) Concentrations are in µg/L, except where noted.

(3) U.S. EPA. *Appendix A to Part 136 Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater Method 608—Organochlorine Pesticides and PCBs*. July 1995.

(4) U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. EPA/600/4-79/020. EMSL-Cincinnati. 1983.

(5) The actual Reporting Limit will depend on the volume of sample filtered.

Notes:

RL = reporting limit.
MDL = Method Detection Limit.
µg/L = micrograms per liter.
mg/L = milligrams per liter.
PCBs = polychlorinated biphenyls.

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)
INORGANICS (METALS AND WET CHEMISTRY)							
Aluminum	7429905	1,000	-	1,000,000,000	1,000	500	30
Antimony	7440360	4,300	-	49,000,000	300	50	7
Arsenic	7440382	4,600	-	2,000,000	100	50	3
Barium	7440393	130,000	-	1,000,000,000	1,000	50	2
Beryllium	7440417	51,000	-	1,000,000,000	500	50	2
Cadmium	7440439	6,000	-	230,000,000	200	50	1
Chromium (Total) [6]	7440473	3,300	-	140,000,000	2,000	50	3
Cobalt	7440484	800	-	48,000,000	500	50	1
Copper	7440508	5,802,000	-	1,000,000,000	1,000	50	3
Iron	7439896	6,000	-	1,000,000,000	5,000	500	70
Lead	7439921	400,000	-	100,000,000	1,000	50	1
Magnesium	7439954	8,000,000	-	6,700,000,000	4,000	5,000	20
Manganese	7439965	1,000	-	180,000,000	1,000	50	2
Mercury (total)	7439976	50	-	20,000,000	50	2,000	NA
Nickel	7440020	100,000	-	1,000,000,000	1,000	50	6
Selenium	7782492	400	-	130,000,000	200	50	10
Silver	7440224	100	-	200,000,000	100	50	4
Sodium	17341252	2,500,000	-	1,000,000,000	10,000	5,000	100
Thallium	7440280	2,300	-	15,000,000	500	50	1
Vanadium	7440622	72,000	-	1,000,000,000	1,000	50	20
Zinc	7440666	2,400,000	-	1,000,000,000	1,000	500	30
Cyanide	57125	100	-	250,000	100	400	NA
Ammonia-N (U.S. EPA 350.1)	7664-41-7	10,000,000	-	6,700,000,000	1,000	500	40
Nitrate-N (U.S. EPA 300.0)	14797-55-8	200,000	-	1,000,000,000	--	100	4
Nitrite-N (U.S. EPA 300.0)	14797-65-0	20,000	-	380,000,000	--	100	2

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)
Total phosphorus as P (U.S. EPA 365.3)	7723140	1,300,000	-	1,000,000,000	--	100	NA

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)
POLYCHLORINATED BIPHENYLS (PCBs)							
Total PCBs	1336363	240,000	-	7,900,000	330	20	NA[5]
Aroclor-1016	12674112		Part 201 N/A		-	10	NA[5]
Aroclor-1221	11104282		Part 201 N/A		-	20	NA[5]
Aroclor-1232	11141165		Part 201 N/A		-	10	NA[5]
Aroclor-1242	53469219		Part 201 N/A		-	10	NA[5]
Aroclor-1248	12672296		Part 201 N/A		-	10	NA[5]
Aroclor-1254	11097691		Part 201 N/A		-	10	NA[5]
Aroclor-1260	11096825		Part 201 N/A		-	10	NA[5]
VOLATILE ORGANIC COMPOUNDS							
1,1,1-Trichloroethane	71556	4,000	-	67,000,000,000	50	50.00	11.10
1,1,2,2-Tetrachloroethane	79345	170	-	54,800,000	50	50.00	13.80
1,1,2-Trichloroethane	79005	100	-	190,000,000	50	50.00	10.40
1,1-Dichloroethane	75343	15,000	-	33,000,000,000	50	50.00	9.06
1,1-Dichloroethylene	75354	62	-	62,000,000	50	50.00	19.80
1,2,4-Trichlorobenzene	120821	1,800	-	25,000,000,000	330	200.00	21.80
1,2-Dibromoethane (ethylene dibromide)	106934	20	-	14,000,000	20	200.00	0.73
1,2-Dichlorobenzene	95501	360	-	100,000,000,000	100	50.00	8.47
1,2-Dichloroethane	107062	100	-	120,000,000	50	50.00	11.40
1,2-Dichloropropane	78875	100	-	270,000,000	50	50.00	19.00
1,3-Dichlorobenzene	541731	170	-	170,000	100	50.00	10.20
1,4-Dichlorobenzene	106467	290	-	570,000,000	100	50.00	8.69
2-Butanone (MEK)	78933	44,000	-	67,000,000,000	750	2,000.00	322.00
2-Hexanone	591786	20,000	-	2,700,000,000	2,500	2,000.00	396.00
4-Methyl-2-pentanone (MIBK)	108101	36,000	-	140,000,000,000	2,500	2,000.00	340.00
Acetone	67641	15,000	-	390,000,000,000	1,000	2,000.00	240.00
Benzene	71432	100	-	470,000,000	50	50.00	10.50

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)
Bromodichloromethane	75274	1,200	-	110,000,000	100	50.00	8.70
Bromoform	75252	1,600	-	3,600,000,000	100	50.00	27.90
Bromomethane	74839	200	-	330,000,000	200	50.00	21.70
Carbon disulfide	75150	16,000	-	47,000,000,000	250	50.00	15.90
Carbon tetrachloride	56235	100	-	170,000,000	50	50.00	13.00
Chlorobenzene	108907	940	-	4,700,000,000	50	50.00	9.33
Chloroethane	75003	8,600	-	670,000,000,000	250	50.00	17.30
Chloroform	67663	1,600	-	1,600,000,000	50	50.00	9.58
Chloromethane	74873	2,300	-	4,900,000,000	250	50.00	13.60
cis-1,2-Dichloroethylene	156592	1,400	-	2,300,000,000	50	50.00	11.60
cis-1,3-Dichloropropene	542756	170	-	780,000,000	100	50.00	8.90
Dibromochloromethane	124481	1,600	-	160,000,000	100	50.00	8.17
Dibromochloropropane	96128	10	-	13,000,000	10	200.00	99.10
Dichlorodifluoromethane	75718	95,000	-	3,300,000,000,000	250	50.00	16.60
Ethylbenzene	100414	360	-	13,000,000,000	50	50.00	9.74
Isopropyl benzene	98828	91,000	-	5,800,000,000	250	200.00	9.30
Methylene chloride	75092	100	-	8,300,000,000	100	200.00	19.30
Methyl-tert-butyl ether (MTBE)	1634044	800	-	200,000,000,000	250	50.00	15.00
Styrene	100425	2,200	-	6,900,000,000	50	50.00	9.43
Tetrachloroethylene	127184	100	-	6,800,000,000	50	50.00	14.00
Toluene	108883	2,800	-	27,000,000,000	100	50.00	9.75
trans-1,2-Dichloroethylene	156605	2,000	-	4,700,000,000	50	50.00	13.90
trans-1,3-Dichloropropene	542756	170	-	780,000,000	100	50.00	9.10
Trichloroethylene	79016	100	-	2,300,000,000	50	50.00	18.80
Trichlorofluoromethane	75694	52,000	-	3,800,000,000,000	100	50.00	17.00
Vinyl chloride	75014	40	-	890,000,000	40	50.00	21.10
m,p-Xylenes	1330207	700	-	290,000,000,000	150	50.00	18.60

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)
o-Xylenes	1330207	700	-	290,000,000,000	150	50.00	7.85
SEMI-VOLATILE ORGANIC COMPOUNDS							
2,4,5-Trichlorophenol	95954	39,000	-	23,000,000,000	330	330	20
2,4,6-Trichlorophenol	88062	330	-	1,300,000,000	330	330	13
2,4-Dichlorophenol	120832	380	-	5,100,000,000	330	330	20
2,4-Dimethylphenol	105679	7,400	-	4,700,000,000	330	330	63
2,4-Dinitrotoluene	121142	430	-	20,000,000	330	330	27
2-Chlorophenol	95578	440	-	19,000,000	330	330	20
2-Methylnaphthalene	91576	57,000	-	37,000,000	330	330	30
2-Methylphenols (J)	1319773	1,400	-	6,700,000,000	330	330	23
2-Nitrophenol	88755	400	-	2,900,000	330	330	20
3,3-Dichlorobenzidine	91941	2,000	-	8,200,000	2,000	330	100
4,6-Dinitro-2-methylphenol (2-methyl-4,6-dinitrophenol)	534521	830	-	360,000	830	330	20
4-Chloro-3-methylphenol	59507	280	-	20,000,000	280	330	20
4-Methylphenol (J)	1319773	1,400	-	6,700,000,000	330	330	23
Acenaphthene	83329	4,400	-	14,000,000,000	330	330	20
Acenaphthylene	208968	5,900	-	2,300,000,000	330	330	17
Anthracene	120127	41,000	-	67,000,000,000	330	330	17
Benzo(a)anthracene	56553	20,000	-	160,000	330	330	10
Benzo(a)pyrene	50328	2,000	-	1,900,000	330	330	13
Benzo(b)fluoranthene	205992	20,000	-	160,000	330	330	17
Benzo(g,h,i)perylene	191242	2,500,000	-	800,000,000	330	330	7
Benzo(k)fluoranthene	207089	200,000	-	1,600,000	330	330	20
bis(2-Chloroethyl)ether (I)	111444	100	-	12,000,000	100	330	37
bis(2-Ethylhexyl)phthalate	117817	2,800,000	-	890,000,000	330	330	30
Butyl benzyl phthalate	85687	26,000	-	47,000,000,000	330	330	23

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)			PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)
Carbazole	86748	1,100	-	3,400,000	330	330	40
Chrysene	218019	2,000,000	-	16,000,000	330	330	13
Dibenzo(a,h)anthracene	53703	2,000	-	16,000	330	330	7
Dibenzofuran	132649		1,700		330	330	23
Diethyl phthalate	84662	2,200	-	3,300,000,000	330	330	17
Dimethyl phthalate	131113	790,000	-	3,300,000,000	330	330	17
Di-n-butylphthalate	84742	11,000	-	3,300,000,000	330	330	10
Di-n-octyl phthalate	117840	6,900,000	-	140,000,000	330	330	13
Fluoranthene	206440	5,500	-	9,300,000,000	330	330	27
Fluorene	86737	5,300	-	9,300,000,000	330	330	30
Hexachlorobenzene (C-66)	118741	350	-	8,500,000	330	330	23
Hexachlorobutadiene (C-46)	87683	91	-	180,000,000	50	330	40
Hexachlorocyclopentadiene (C-56)	77474	30,000	-	13,000,000	330	330	330
Hexachloroethane	67721	430	-	230,000,000	300	330	33
Indeno(1,2,3-cd)pyrene	193395	20,000	-	160,000	330	330	7
Isophorone	78591	11,000	-	12,000,000,000	330	330	17
Naphthalene	91203	870	-	200,000,000	330	330	27
Nitrobenzene (I)	98953	330	-	47,000,000	330	330	37
n-Nitroso-di-n-propylamine	621647	330	-	2,000,000	330	330	23
N-Nitrosodiphenylamine	86306	5,400	-	11,000,000	330	330	53
Pentachlorophenol	87865	22	-	130,000,000	20	330	30
Phenanthrene	85018	5,300	-	7,200,000	330	330	17
Phenol	108952	4,200	-	40,000,000,000	330	330	23
Pyrene	129000	480,000	-	6,700,000,000	330	330	40

QAPP Worksheet #15-2
Reference Limits and Evaluation (Soil/Sediment)

PARAMETER[1][4]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µg/kg)	PART 201 TDLs (µg/kg)	QUANTITATION LIMIT[2] (µg/kg)	METHOD DETECTION LIMIT[2] (µg/kg)

Notes:
[1] The parameters included in this table are those included in the USEPA Contract Laboratory Program (CLP) Target Compound List (TCL) and Target Analyte List (TAL), except those that are not on the Part 201 list; Calcium, Potassium, 1,2,3-Trichlorobenzene, Bromochloromethane, Cyclohexane, Methyl Acetate, Methylcyclohexane (methyl phenol), 1,1-Biphenyl, 2,2-oxybis(1-Chloropropane), 2,4-Dinitrophenol, 2,6-Dinitrotoluene, 2-Nitroaniline, 3-Nitroaniline, 4-Bromophenyl-phenylether, 4-Chloroaniline, 4-Chlorophenyl-phenylether, 4-Nitroaniline, 4-Nitrophenol, Benzaldehyde, bis(2-Chloroethoxy)methane. Or those that are not typically analyzed by WATS or CAS: 1,1,2-Trichloro-1,2,2-triflouroethane, 1,2,4,5-Tetrachlorobenzene, Acetophenone, Atrazine, beta-Chloronaphthalene, Caprolactum.

[2] The actual Quantitation Limits and Method Detection Limits will vary with sample size, for the analysis of PCBs and PAHs.
[3] Potentially applicable Michigan Part 201 Criteria are from the Michigan Department of Environmental Quality (MDEQ) Remediation and Redevelopment Division (RRD) Operational Memorandum No. 1, dated January 23, 2006.
[4] VOC analysis will be conducted by Columbia Analytical Services. All other analyses will be conducted by Weyerhaeuser Analytical Testing Services
[5] The MDL actually achievable in a given analysis will vary depending on detector response characteristics, irreducible noise from instrument electronics, and matrix effects.
[6] The Michigan Part 201 Criteria for Hexavalent Chromium will be used for Chromium (total) as there is no total chromium criteria established.
WATS = Weyerhaeuser Analytical Testing Service.
NA = Not Available
NS = no standard.

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)			PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)
METALS (TOTAL/SPLP) AND CYANIDE							
Aluminum	7429905	50	-	64,000,000	50	5	0.3
Antimony	7440360	6	-	68,000	2	0.5	0.07
Arsenic	7440382	10	-	4,300	5	0.5	0.03
Barium	7440393	2,000	-	14,000,000	100	0.5	0.02
Beryllium	7440417	4	-	290,000	1	0.5	0.02
Cadmium	7440439	5	-	190,000	1	0.5	0.01
Chromium (Total) [6]	7440473	11	-	460,000	10	0.5	0.03
Cobalt	7440484	40	-	2,400,000	20	0.5	0.008
Copper	7440508	1,000	-	7,400,000	4	0.5	0.03
Iron	7439896	300	-	58,000,000	200	0.5	0.7
Lead	7439921	-	4	-	3	0.5	0.006
Magnesium	7439954	400,000	-	1,000,000,000	1,000	50	0.2
Manganese	7439965	50	-	9,100,000	50	0.5	0.02
Mercury (total)[4]	7439976	0.0013	-	56	0.001	1 (ng/L)	0.06 (ng/L)
Methyl Mercury [4]	22967926	0.0013	-	56	0.001	0.1 (ng/L)	0.05 (ng/L)
Nickel	7440020	100.00	-	74,000,000	20	0.5	0.06
Selenium	7782492	5	-	970,000	5	0.5	0.1
Silver	7440224	0.2	-	1,500,000	0.2	0.5	0.04
Sodium	17341252	120,000	-	1,000,000,000	1,000	50	1
Thallium	7440280	2	-	13,000	2	0.5	0.007
Vanadium	7440622	5	-	970,000	4	0.5	0.2
Zinc	7440666	2,400	-	110,000,000	50	5	0.3
Cyanide	57125	5	-	57,000	5	9	3

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)			PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)
POLYCHLORINATED BIPHENYLS (PCBs)							
Total PCBs	1336363	0.2	-	45	0.2	0.2	NA[5]
Aroclor-1016	12674112		Part 201 N/A			0.2	NA[5]
Aroclor-1221	11104282		Part 201 N/A			0.2	NA[5]
Aroclor-1232	11141165		Part 201 N/A			0.2	NA[5]
Aroclor-1242	53469219		Part 201 N/A			0.2	NA[5]
Aroclor-1248	12672296		Part 201 N/A			0.2	NA[5]
Aroclor-1254	11097691		Part 201 N/A			0.2	NA[5]
Aroclor-1260	11096825		Part 201 N/A			0.2	NA[5]
VOLATILE ORGANIC COMPOUNDS							
1,1,1-Trichloroethane	71556	200	-	1,300,000	1	0.5	0.13
1,1,2,2-Tetrachloroethane	79345	9	-	77,000	1	0.5	0.09
1,1,2-Trichloroethane	79005	5	-	110,000	1	0.5	0.10
1,1-Dichloroethane	75343	740	-	2,400,000	1	0.5	0.09
1,1-Dichloroethylene	75354	7	-	140,000	1	0.5	0.08
1,2,4-Trichlorobenzene	120821	30	-	300,000	5	0.5	0.07
1,2-Dibromoethane (ethylene dibromide)	106934	0.05	-	15,000	0.05	0.5	0.11
1,2-Dichlorobenzene	95501	16	-	160,000	1	0.5	0.06
1,2-Dichloroethane	107062	5	-	2,500,000	1	0.5	0.12
1,2-Dichloropropane	78875	5	-	2,800,000	1	0.5	0.09
1,3-Dichlorobenzene	541731	7	-	2,000	1	0.5	0.09
1,4-Dichlorobenzene	106467	13	-	74,000	1	0.5	0.11
2-Butanone (MEK)	78933	2,200	-	240,000,000	25	5	0.92
2-Hexanone	591786	1,000	-	8,700,000	50	5	0.84
4-Methyl-2-pentanone (MIBK)	108101	1,800	-	20,000,000	50	5	0.77
Acetone	67641	730	-	1,000,000,000	50	5	0.74
Benzene	71432	5	-	68,000	1	0.5	0.10

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)			PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)
Bromodichloromethane	75274	80	-	37,000	1	0.5	0.08
Bromoform	75252	80	-	3,100,000	1	0.5	0.09
Bromomethane	74839	10	-	70,000	5	0.5	0.21
Carbon disulfide	75150	800	-	1,200,000	5	0.5	0.09
Carbon tetrachloride	56235	5	-	9,600	1	0.5	0.09
Chlorobenzene	108907	47	-	470,000	1	0.5	0.08
Chloroethane	75003	430	-	5,700,000	5	0.5	0.09
Chloroform	67663	80	-	180,000	1	0.5	0.07
Chloromethane	74873	260	-	490,000	5	0.5	0.15
cis-1,2-Dichloroethylene	156592	70	-	530,000	1	0.5	0.09
cis-1,3-Dichloropropene	542756	8.5	-	130,000	1	0.5	0.16
Dibromochloromethane	124481	80	-	110,000	5	0.5	0.09
Dibromochloropropane	96128	0.2	-	1,200	0.2	0.5	0.26
Dichlorodifluoromethane	75718	1,700	-	300,000	5	0.5	0.12
Ethylbenzene	100414	18	-	170,000	1	0.5	0.10
Isopropyl benzene	98828	800	-	56,000	5	0.5	0.15
Methylene chloride	75092	5	-	1,400,000	5	0.5	0.04
Methyl-tert-butyl ether (MTBE)	1634044	40	-	47,000,000	5	0.5	0.12
Styrene	100425	80	-	310,000	1	0.5	0.07
Tetrachloroethylene	127184	5	-	200,000	1	0.5	0.12
Toluene	108883	140	-	530,000	1	0.5	0.09
trans-1,2-Dichloroethylene	156605	100	-	230,000	1	0.5	0.11
trans-1,3-Dichloropropene	542756	8.5	-	130,000	1	0.5	0.15
Trichloroethylene	79016	5	-	1,100,000	1	0.5	0.10
Trichlorofluoromethane	75694	2,600	-	1,100,000	1	0.5	0.08
Vinyl chloride	75014	2	-	33,000	1	0.5	0.06
m,p-Xylene	1330207	35	-	190,000	3	0.5	0.27

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)			PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)
o-Xylene	1330207	35	-	190,000	3	0.5	0.12
SEMI VOLATILE ORGANIC COMPOUNDS							
2,4,5-Trichlorophenol	95954	730	-	170,000	5	10	0.6
2,4,6-Trichlorophenol	88062	4.4	-	10,000	4	10	0.4
2,4-Dichlorophenol	120832	19	-	48,000	10	10	0.6
2,4-Dimethylphenol	105679	370	-	520,000	5	10	1.9
2,4-Dinitrotoluene	121142	7.7	-	8,600	5	10	0.8
2-Chlorophenol	95578	22	-	94,000	10	10	0.6
2-Methylnaphthalene	91576	260	-	25,000	5	10	0.9
2-Methylphenol (J)	1319773	71	-	810,000	10	10	0.7
2-Nitrophenol	88755	20	-	79,000	5	10	0.6
3,3-Dichlorobenzidine	91941	0.3	-	180	0.3	10	3
4,6-Dinitro-2-methylphenol (2-methyl-4,6-dinitrophenol)	534521	20	-	9,500	20	10	0.6
4-Chloro-3-methylphenol	59507	7.4	-	79,000	5	10	0.6
4-Methylphenol (J)	1319773	71	-	810,000	10	10	0.7
Acenaphthene	83329	19	-	4,200	5	10	0.6
Acenaphthylene	208968	52	-	3,900	5	10	0.5
Anthracene	120127		43		5	10	0.5
Benzo(a)anthracene	56553	2.1	-	9.4	1	10	0.3
Benzo(a)pyrene	50328	1	-	5	1	10	0.4
Benzo(b)fluoranthene	205992		1.5		1	10	0.5
Benzo(g,h,i)perylene	191242		1		1	10	0.2
Benzo(k)fluoranthene	207089		1		1	10	0.6
bis(2-Chloroethyl)ether (I)	111444	1	-	17,000,000	1	10	1.1
bis(2-Ethylhexyl)phthalate	117817	6	-	340	5	10	0.9
Butyl benzyl phthalate	85687	14	-	2,700	5	10	0.7

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)			PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)
Carbazole	86748	10	-	7,400	10	10	1.2
Chrysene	218019		1.6		1	10	0.4
Dibenzo(a,h)anthracene	53703		2		2	10	0.2
Dibenzofuran	132649		4		4	10	0.7
Diethyl phthalate	84662	110	-	1,100,000	5	10	0.5
Dimethyl phthalate	131113	73,000	-	4,200,000	5	10	0.5
Di-n-butylphthalate	84742	9.7	-	11,000	5	10	0.3
Di-n-octyl phthalate	117840	130	-	400	5	10	0.4
Fluoranthene	206440	1.6	-	210	1	10	0.8
Fluorene	86737	12	-	2,000	5	10	0.9
Hexachlorobenzene (C-66)	118741	0.2	-	3,000	0.2	10	0.7
Hexachlorobutadiene (C-46)	87683	0.05	-	3,200	0.05	10	1.2
Hexachlorocyclopentadiene (C-56)	77474	50	-	1,600	5	10	10
Hexachloroethane	67721	6.7	-	50,000	5	10	1
Indeno(1,2,3-cd)pyrene	193395		2		2	10	0.2
Isophorone	78591	570	-	12,000,000	5	10	0.5
Naphthalene	91203	13	-	31,000	5	10	0.8
Nitrobenzene (I)	98953	3.4	-	550,000	3	10	1.1
n-Nitroso-di-n-propylamine	621647	5	-	360	5	10	0.7
N-Nitrosodiphenylamine	86306	270	-	35,000	5	10	1.6
Pentachlorophenol	87865	1	-	200	1	10	0.9
Phenanthrene	85018	2.4	-	1,000	2	10	0.5
Phenol	108952	210	-	29,000,000	5	10	0.7
Pyrene	129000		140		5	10	1.2

QAPP Worksheet #15-3
Reference Limits and Evaluation (Groundwater)

PARAMETER[1]	CHEMICAL ABSTRACT SERVICE NUMBER	RANGE OF POTENTIALLY APPLICABLE PART 201 CRITERIA[3] (µG/L)	PART 201 TARGET DETECTION LIMIT (µG/L)	AQUEOUS QUANTITATION LIMIT[2] (µG/L)	METHOD DETECTION LIMIT[2] (µG/L)

Notes:
[1] The parameters included in this table are those included in the USEPA Contract Laboratory Program (CLP) Target Compound List (TCL) and Target Analyte List (TAL), except those that are not on the Part 201 list Calcium, Potassium, 1,2,3-Trichlorobenzene, Bromochloromethane, Cyclohexane, Methyl Acetate, Methylcyclohexane (methyl phenol), 1,1-Biphenyl, 2,2-oxybis(1-Chloropropane), 2,4-Dinitrophenol, 2,6-Dinitrotoluene, 2-Nitroaniline, 3-Nitroaniline, 4-Bromophenyl-phenylether, 4-Chloroaniline, 4-Chlorophenyl-phenylether, 4-Nitroaniline, 4-Nitrophenol, Benzaldehyde, bis(2-Chloroethoxy)methane. Or those that are not typically analyzed by WATS or CAS: 1,1,2-Trichloro-1,2,2-triflouroethane, 1,2,4,5-Tetrachlorobenzene, Acetophenone, Atrazine, beta-Chloronaphthalene, Caprolactum.
[2] The actual Quantitation Limits and Method Detection Limits will vary with sample size, for the analysis of PCBs and PAHs.
[3] Potentially applicable Michigan Part 201 Criteria are from the Michigan Department of Environmental Quality (MDEQ) Remediation and Redevelopment Division (RRD) Operational Memorandum No. 1, dated December 10, 2004.
[4] Low level and methyl mercury will be analyzed by Columbia Analytical Services (CAS).
[5] The MDL actually achievable in a given analysis will vary depending on detector response characteristics, irreducible noise from instrument electronics, and matrix effects.
[6] The Michigan Part 201 Criteria for Hexavalent Chromium will be used for Chromium (total) as there is no total chromium criteria established.
WATS = Weyerhaeuser Analytical Testing Service.
NA = Not Available
NS = no standard.

QAPP Worksheet #15-4
Reference Limits and Evaluation (Free Product)

ANALYTE	CAS NUMBER	PROJECT ACTION LIMIT[1]	FREE PRODUCT (µg/L)[2]	
			LABORATORY MDL	LABORATORY RL
PCBs (U.S. EPA 8082)				
Aroclor - 1016	12674-11-2	--	0.20	0.2
Aroclor - 1221	11104-28-2	--	--	0.2
Aroclor - 1232	11141-16-5	--	0.30	0.2
Aroclor - 1242	53469-21-9	--	0.24	0.2
Aroclor - 1248	12672-29-6	--	0.33	0.2
Aroclor - 1254	11097-69-1	--	0.25	0.2
Aroclor - 1260	11096-82-5	--	0.24	0.2
Total PCBs	1336-36-3	0.2 µg/L	--	0.2
Physical Properties				
Viscosity (ASTM D445)	--	--	--	--
Specific Gravity (ASTM D287)	--	--	--	--

Footnotes:
(1) Standards are consistent with the Multi-Area Quality Assurance Project Plan (Rev. 00) For the Kalamazoo River Study Group (Arcadis BBL, 2007b), which are from the MDEQ's Substantive Requirements Document for the Plainwell Dam Superfund Site, dated February 13, 2007. The TSS standards are on a monthly and daily basis, respectively.
(2) Concentrations are in µg/L, except where noted.

Notes:
RL = reporting limit.
MDL = Method Detection Limit.
µg/L = micrograms per liter.
mg/L = milligrams per liter.
PCBs = polychlorinated biphenyls.

QAPP Worksheet #16-5
Project Schedule/Timeline
Plainwell Mill Phase II RI Work Plan

ACTIVITIES	ORGANIZATION	DATES (MM/DD/YY)		DELIVERABLE	DELIVERABLE DUE DATE
		ANTICIPATED DATE(S) OF INITIATION	ANTICIPATED DATE OF COMPLETION		
Implementation of the Phase II RI	CRA	07/08/09	09/25/09	RI Report	80 Days After Completion of Field Activities and Notice to the U.S. EPA
Identification of Remedial Action Objectives	CRA	01/01/10	02/18/10	Screening Report	70 Days After U.S. EPA approval of the Draft
Feasibility Study	CRA	05/28/10	10/28/10	Feasibility Study Report	110 Days After U.S. EPA approval of the Draft

QAPP Worksheet #16-6
Project Schedule/Timeline
12th Street Landfill RA Work Plan

ACTIVITIES	ORGANIZATION	DATES (MM/DD/YY)		DELIVERABLE	DELIVERABLE DUE DATE
		ANTICIPATED DATE(S) OF INITIATION	ANTICIPATED DATE OF COMPLETION		
Completion of Remedial Design	CRA	04/22/09	07/20/09	Submittal 1[1], Submittal 2 and Final Submittal[2]	57 Days After Completion of Remedial Design Completion
RA Work Plan	CRA	06/08/09	07/31/09	RA Work Plan Report	39 Days After submitting Submittals to U.S. EPA
Preliminary RA Implementation 2009 Construction Work	CRA	07/08/09	11/13/09	NA	NA
Preliminary RA Implementation 2010 Construction Work	CRA	04/05/10	10/06/10	Certification of Completion of Construction Report	In Accordance with RA Work Plan

(1) Submittal 1 was provided to U.S. EPA on May 27, 2009.

(2) Final Submittal will include all required elements at a final level of detail

QAPP Worksheet #17-5
Sampling Design and Rationale
Plainwell Mill Phase II RI Work Plan

Describe and provide a rationale for choosing the sampling approach (*e.g.*, grid system, biased statistical approach):

Surface Water Quality:

The surface water sample will be collected at a location near the southeast of the mill at millrace and one at a location near northeast of the mill at the Kalamazoo River as described in Worksheet #11. The samples will be analyzed to characterize the surface water quality and to determine the analytical needed for data comparison.

Soil Sampling Activities:

Soil samples will be collected at various locations/depths to further characterize the soil at the mill and to confirm the historical exceedances at some locations/depths.

Groundwater Monitoring:

Site-wide groundwater monitoring will be performed at existing and new monitoring locations to further evaluate the groundwater beneath the site, confirm the historical exceedances, and to determine the next steps in investigation activities.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations):

Refer to Worksheet #18-5.

QAPP Worksheet #17-6
Sampling Design and Rationale
12Th Street Landfill RA Work Plan

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach):

Asphalt Plant Property Soil Sampling:

The collected soil samples will be submitted to laboratory for a quick-turn analysis (24 to 72 hour) so the results can be reviewed and the adequacy of the excavation can be verified before restoring the excavated area.

MDNR Properties Soil Sampling:

The collected soil samples will be submitted to laboratory for a quick-turn analysis (24 to 72 hour) so the results can be reviewed and the adequacy of the excavation can be verified before restoring the excavated area.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations):

Refer to Worksheet #18-6.

QAAP Worksheet # 18-4
Sampling Locations and Methods/SOP Requirments
Plainwell mill Phase II RI Work Plan

ACTIVITY/ LOCATION	PROPOSED ASSESSMENT LOCATION			RATIONALE FOR LOCATION SELECTION	SAMPLE/DATA COLLECTION DETAILS	CONCENTRATION LEVEL	SAMPLE MATRIX	FIELD PARAMETERS	SAMPLING SOP REFERENCE[3]	LABORATORY PARAMETERS	SAMPLE LOCATIONS	INVESTIGATIVE SAMPLES	QUALITY CONTROL SAMPLES			TOTAL NUMBER OF SAMPLES
	DESIGNATION	TYPE	DEPTH (FT BGS)										FIELD BLANKS	FIELD DUPLICATES	MS/MSD. MS/DUP	
Soil Sampling																
DG3 and DG4	SB-301, SB-302	Soil Boring	20	Confirmation of potential contamination noted in historical sampling	-Collection of one soil sample from what is field screened to be clean soils (one from upper unit, one from lower unit) -Collection of one soil sample from what is field screened as contaminated soils	Not applicable	Soil	PID Screening	F-5	TCL VOCs. TCL SVOCs TAL Metals SPLP Metals [1] PCBs General Chemistry [2]	2	6	--	--	--	7
SGWB-10	MW-18	Monitoring Well	20								1	3	--	--	--	3
SGWB-3	SB-321	Soil Boring	20								1	3	--	1	--	4
Coal Pile Storage Area	SB-303 SB-304 SB-305 SB-306 SB-307 SB-308 SB-309 SB-310	Soil Boring	5	Confirmation of extent of coal impacts	-Collection of soil samples which are field screened to be clean below any noted potential contamination		Soil	PID Screening			8	8	--	1	1	10
No. 6 Fuel Oil Tank Area	SB-311 SB-312 SB-313 SB-314 SB-315	Soil Boring	10	Confirmation of impacted soil removal activities	-Collection of one soil sample from what is field screened to be clean soils (one from upper unit, one from lower unit) -Collection of one soil sample from what is field screened as contaminated soils		Soil	PID Screening			5	15	--	1	--	16
SGWA-5	MW-19	Monitoring Well	20	Confirmation of historical groundwater impacts	-Collection of soil samples which is field screened to be clean below any noted potential contamination		Soil	PID Screening			1	1	--	--	--	1
Former Coal Tunnel	SB-316 SB-317 SB-318 SB-319 SB-320	Soil Boring	10	Confirmation of potential contamination noted in historical sampling	-Collection of soil samples which is field screened to be clean below any noted potential contamination		Soil	PID Screening			4	4	--	1	1	6
Groundwater Sampling																
MW-6, MW-7, MW-18, MW-19	--	Groundwater Sample	--	Confirmation of on-Site groundwater chemistry	-Completion of a monitoring well inspection -Collection of groundwater and surface water levels (at associated staff gauges) -Collection of one groundwater sample per location	Normal	Groundwater	pH, Conductivity, Temperature, Dissolved Oxygen, ORP, Turbidity	F-11	TCL VOCs TCL SVOCs PCBs TAL Inorganics	5	5	1	1	1	8

Notes

- Collect soil samples on a continuous basis at 2 foot intervals
- Collection of all samples as per Field Sampling Plan and Quality Assurance Project Plan
- Samples to be submitted on a regular turn around time. Indicate all detection limits on chain of custody.

(1) SPLP (Synthetic Precipitation Leaching Procedure) will be collected and placed on hold pending results from TAL metals analysis.
(2) General Chemistry- Nitrogen compounds and phosphorous
(3) See Project Sampling SOP References table (Worksheet #21).

- TAL Inorganics- TAL Metals plus Low level mercury, methly mercury, and cyanide

* Sampling to be conducted if necessary, the noted amount of locations is subject to change depending on findings.
All necessary MS/MSD and Field Dups will be added if needed.

QAPP Worksheet #18-5
Sampling Locations and Methods/SOP Requirements
12TH Street Landfill RA Work Plan

SAMPLING LOCATION/ID NUMBER	MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	NUMBER OF SAMPLES[2] (identify field duplicates)	SAMPLING SOP REFERENCE[1]	RATIONALE FOR SAMPLING LOCATIONS
Asphalt Plant Property	Soil	Total PCBs	Not applicable	Nine samples, one filed duplicates and one MS/MSDS sample will be collected, the exact number of samples and QA/QC samples to be collected will be determine following completion of excavation activities.	F-6	The results of the sampling activities will verify the adequacy of the excavation limits before restoring the excavation area.
		TCL VOCs	Not applicable		F-6	The results of the sampling activities will verify the adequacy of the excavation limits before restoring the excavation area.
MDNR Properties	Soil	Total PCBs	Not applicable	13 samples, one filed duplicates and one MS/MSDS sample will be collected, the exact number of samples and QA/QC samples to be collected will be determine following completion of excavation activities.	F-6	Surface samples (*i.e.*, 0 to 6 inches) obtained to verify removal effectiveness

Footnotes:

(1) See Project Sampling SOP References table (Worksheet #21).

(2) Field duplicates will be collected at a frequency of one duplicate for every 10 samples (Worksheet #20).

QAPP Worksheet #19
Analytical SOP Requirements

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	ANALYTICAL AND PREPARATION METHOD/SOP REFERENCE[1]	SAMPLE VOLUME	CONTAINERS (number, size, and type)	PRESERVATION REQUIREMENTS (chemical, temperature, light protected)	MAXIMUM HOLDING TIME (preparation/ analysis)
Water	PCBs	All	W-1 (AM E-608)	2 liters	Two 1-liter amber glass bottles with Teflon®-lined lid	Cool to 4°C ±2°	14 days to extraction; 40 days to analysis
Water	TSS	All	W-2, W-5 (AM E-160.2) (AQ-O-DLYCHK)	1 liter	One 1-liter plastic container	Cool to 4°C ±2°	7 days to analysis
Water	Total phosphorus	All	W-3 (AM E-365.3)	500 mL	One 500-mL plastic container	H_2SO_4 to pH<2; cool to 4°C	28 days to analysis
Water	TAL metals (total)	All	W-14 (AM E-200.8M)	500 mL	1 x 1,000-mL high-density polyethylene bottle	Cool to 4°C, add nitric acid to pH <2	6 months
Water	Total cyanide and amenable cyanide	All	W-25 (AM E-335.2 CLP-M)	500 ml	1 x 500 ml plastic bottle	Sodium Hydroxide to pH ≤ 12; Cool to 4°C	14 days
Water	Low-level mercury (total)	All	C-4 (MET-1631)	500 mL	1 x 500-mL fluorinated LPE bottle	Add HCl to pH <2, 2.5 mL of BrCl is added at laboratory	48 hrs unpreserved; 90 days preserved to analysis.
Water	Methyl Mercury	All	C-7 (MET-1630W)	500 mL	1 x 500 mL fluorinated plastic bottle	Dark, Cool to 4°C, add HCl to pH <2, in clean polyethylene bag	180 days to analysis
Water	SVOCs	All	W-15 (AM E-8270)	1,000 mL	2 x 1,000-mL amber glass bottle, Teflon®-lined cap	Cool to 4°C; protect from light	Extract within 7 days; analyze within 40 days of extraction
Water	VOCs	All	W-21 (AM E-8260)	1 x 40 mL VOA vial	3 x 40-mL glass VOA vials with Teflon® septum	Cool to 4°C, add HCl to pH <2; protect from light	14 days (sample should remain on-site less than 24 hours)

QAPP Worksheet #19
Analytical SOP Requirements

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	ANALYTICAL AND PREPARATION METHOD/SOP REFERENCE[1]	SAMPLE VOLUME	CONTAINERS (number, size, and type)	PRESERVATION REQUIREMENTS (chemical, temperature, light protected)	MAXIMUM HOLDING TIME (preparation/ analysis)
Water	Hardness	All	W-26 (AM S-2340B)	500 mL	1 x 1,000-mL high-density polyethylene bottle	Cool to 4°C, add nitric acid to pH <2	6 months
Soil/Sediment	PCBs	All	W-4 (AM-E-8082)	200 grams	One 8-oz glass jar with Teflon®-lined lid	Cool to 4°C ±2°	14 days to extraction; 40 days to analysis
Soil	Metals	All	W-14 (AM E-200.8M)	50 grams	One 500-mL amber glass bottle with Teflon®-lined lid	Cool to 4°C ±2°	6 months
Soil	Cyanide	All	W-25 (AM E-335.2 CLP-M)	10 grams (at least)	One 8-oz wide mouth glass jar	Cool to 4°C ±2°	14 days
Soil	SVOCs	All	W-15 (AM E-8270)	100 grams	One 500-mL amber glass bottle with Teflon®-lined lid	Cool to 4°C ±2°	14 days
Soil	VOCs	All	C-5, C-6 (VOC-8260, VOC-5035)	5 grams	1x40-mL VOA vials	Vial containing 5 ml Methanol, cool to 4°C ±2°	14 days
Soil	GRO, DRO	All	W-22, W-23 (AM U-WTPH-D, AM U-WTPH-G)	100 grams	WTPH-D- One 500-mL amber glass bottle with Teflon®-lined lid. WTPH-G-4 oz jar with Teflon®-lined lid	Cool to 4°C ±2°	14 days
Soil	Ammonia-N	All	C-9 (GEN-350.1)	100 grams	One 500-mL amber glass bottle with Teflon®-lined lid	Cool to 4°C ±2	7 days to extraction; 28 days to analysis (preserved with 9N sulfuric acid)
Soil	Nitrate-N	All	C-8 (GEN-353.2)	50 grams	One 8-oz wide mouth glass jar	Cool to 4°C ±2°	7 days to extraction; 28 days to analysis

QAPP Worksheet #19
Analytical SOP Requirements

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	ANALYTICAL AND PREPARATION METHOD/SOP REFERENCE[1]	SAMPLE VOLUME	CONTAINERS (number, size, and type)	PRESERVATION REQUIREMENTS (chemical, temperature, light protected)	MAXIMUM HOLDING TIME (preparation/ analysis)
Soil	Nitrite-N	All	C-8 (GEN-353.2)	50 grams	One 8-oz wide mouth glass jar	Cool to 4°C ±2°	7 days to extraction; 48 hours to analysis
Soil	Phosphorous-Total	All	C-10 (GEN-365.3)	50 grams	One 8-oz wide mouth glass jar	Cool to 4°C ±2°	28 days
Free product	PCBs	All	S-1	3L	3 x 1L Glass	None	14 days to extraction; 40 days to analysis
Free product	Viscosity	Not Applicable	S-2	1L	1L Plastic	None	None
Free Product	Specific Gravity	Not Applicable	S-3	500 mL	500 mL Plastic	None	None

Footnote:

[1] See the Analytical SOP Reference (Worksheet #23).

QAPP Worksheet #20
Field Quality Control Sample Summary

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	ANALYTICAL AND PREPARATION SOP REFERENCE[1]	NUMBER OF SAMPLING LOCATIONS	NUMBER OF FIELD DUPLICATE PAIRS	MATRIX SPIKES	NUMBER OF TRIP BLANKS	NUMBER OF EQUIPMENT BLANKS	TOTAL NUMBER OF SAMPLES TO LABORATORY
Water	PCB	All	W-1	TBD	1/10	1/20	NA	1/10	TBD
Water	TSS	All	W-2, W-5	TBD	1/10	NA	NA	1/10	TBD
Water	Total phosphorus	All	W-3	TBD	1/10	1/20	NA	1/10	TBD
Water	TAL metals (total)	All	W-14	TBD	1/10	1/20	NA	1/10	TBD
Water	Total cyanide and amenable cyanide	All	W-24	TBD	1/10	1/20	NA	1/10	TBD
Water	Hardness	All	W-26	TBD	1/10	1/20	NA	1/10	TBD
Water	Low-level mercury (total)	All	C-4	TBD	1/10	1/20	TBD	1/10	TBD
Water	Methyl Mercury	All	C-7	TBD	1/10	1/20	NA	1/10	TBD
Water	SVOCs	All	W-15	TBD	1/10	1/20	NA	1/10	TBD
Water	VOCs	All	W-21	TBD	1/10	1/20	TBD	1/10	TBD
Soil/Sediment	PCB	All	W-4	TBD	1/10	1/20	NA	1/10	TBD
Soil	Metals (total/SPLP)	All	W-14, W-25	TBD	1/10	1/20	NA	1/10	TBD
Soil	Ammonia-N	All	C-9	TBD	1/10	1/20	NA	1/10	TBD
Soil	Nitrate-N	All	C-8	TBD	1/10	1/20	NA	1/10	TBD
Soil	Nitrite-N	All	C-8	TBD	1/10	1/20	NA	1/10	TBD
Soil	Phosphorous	All	C-10	TBD	1/10	1/20	NA	1/10	TBD
Soil	SVOCs	All	W-15	TBD	1/10	1/20	NA	1/10	TBD
Soil	VOCs	All	W-21	TBD	1/10	1/20	TBD	1/10	TBD
Soil	GRO, DRO	All	W-22, W-23	TBD	1/10	NA	TBD	1/10	TBD
Free product	PCBs	All	S-1	TBD	1/10	1/20	NA	1/10	TBD

QAPP Worksheet #20
Field Quality Control Sample Summary

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	ANALYTICAL AND PREPARATION SOP REFERENCE[1]	NUMBER OF SAMPLING LOCATIONS	NUMBER OF FIELD DUPLICATE PAIRS	MATRIX SPIKES	NUMBER OF TRIP BLANKS	NUMBER OF EQUIPMENT BLANKS	TOTAL NUMBER OF SAMPLES TO LABORATORY
Free product	Viscosity	Not Applicable	S-2	TBD	NA	NA	NA	NA	NA
Free Product	Specific Gravity	Not Applicable	S-3	TBD	NA	NA	NA	NA	NA

Footnote:
(1) See Analytical SOP Reference (Worksheet #23).

Note:
NA = not applicable.
TBD = to be determined

QAPP Worksheet #21
Project Sampling SOP Reference

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	ORIGINATING ORGANIZATION	EQUIPMENT TYPE	MODIFIED FOR PROJECT WORK? (Y/N)	COMMENTS
F-1	Water Sampling and Field Measurement Procedures	RMT	Kemmerer water sampler, peristaltic pump, automated sampler, appropriate sample containers	Y	Sample method is dependent on water conditions at the sample location and specified analysis required
F-2	Surface Water Flow Measurement Procedures	RMT	electromagnetic velocity meter	Y	--
F-3	Water Treatment System Monitoring Procedures	RMT	appropriate sample containers	Y	--
F-4	Sediment Sampling Procedures	RMT	Trowel, stainless steel scoop, bucket auger, tube auger, coring device	Y	Sample method is dependent of sediment site characteristics
F-5	Soil Sampling Procedures Direct Push Sampler	RMT	--	Y	--
F-6	Surficial Soil Sampling Procedures	RMT	Trowel, stainless steel scoop	--	Confirmation sampling will consist of collecting surficial soil samples
F-7	Soil Gas Monitoring	RMT	Geoprobe® rods utilizing the Post Run Tubing (PRT) system and drive point or its equivalent; tubing; Landtec gas monitor or its equivalent	Y	--

QAPP Worksheet #21
Project Sampling SOP Reference

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	ORIGINATING ORGANIZATION	EQUIPMENT TYPE	MODIFIED FOR PROJECT WORK? (Y/N)	COMMENTS
F-8	Excavation of Test Pits and Test Pit Soil Sampling	RMT	Stainless steel shovels, trowels, spoons, or spatulas. Backhoe Equipment	Y	--
F-9	Photoionization Detector (PID) Screening	RMT	--	Y	--
F-10	Staff Gage Installation and Measurement Procedure	RMT	Stadia rod, circular bubble level, laser level instrument	Y	--
F-11	Groundwater Sampling Procedures	CRA	Bladder pump, peristaltic pump, or its equivalent	Y	--
F-12	Ambient Air Monitoring for Fugitive Dust	RMT	High volume air pump	Y	--
F-13	Ambient Air Monitoring for VOCs	RMT	High volume air pump	Y	--
F-14	Real-Time Turbidity Measurement Procedures for Surface Water	RMT	--	Y	--
F-15	Monitoring Well Installation Procedures	RMT	--	Y	--
F-16	Surface Water Sampling Procedure	CRA	Dip sampler, Kemmerer or Van Dorn bottles, Line and messengers, and Peristaltic pumps	Y	--

QAPP Worksheet #22
Field Equipment Calibration, Maintenance, Testing, and Inspection

FIELD EQUIPMENT	CALIBRATION ACTIVITY	MAINTENANCE ACTIVITY	TESTING ACTIVITY	INSPECTION ACTIVITY	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION	RESPONSIBLE PERSON	SOP REFERENCE[1]
Multi-parameter Water Quality Meter	F-1	Per SOP and manufacturer's specifications	Turbidity, temperature, pH, conductivity, DO	Check membranes and verify accurate operation	Daily	F-1	F-1	F-1	F-1 and Manufacture's Operations Manual
ISCO sampler or equivalent	Verify sample volumes	Battery charging	Collecting appropriate sample volumes	Check battery operation and tubing	Daily	F-1	F-1	F-1	F-1
Landtec gas sampler, or equivalent	F-7	Per manufacturer's specifications	Measuring concentration of methane, carbon dioxide, and oxygen	Check tubing and sample port integrity	Daily	F-7	F-7	F-7	F-7
Magnehelic pressure gauge, or equivalent	F-7	Per manufacturer's specifications	Measuring pressures	Check tubing and sample port integrity	Daily	F-7	F-7	F-7	F-7
Photoionization Detector	F-9	Per manufacturer's specifications	Measuring photoionization in soil	Check sample device	Daily	F-9	F-9	F-9	F-9
Flow-Through Cell	F-11	Per manufacturer's specifications	temperature, turbidity, dissolved oxygen, specific electrical conductance, and pH electrodes	Check sample device	Daily	F-11	F-11	F-11	F-11

QAPP Worksheet #22
Field Equipment Calibration, Maintenance, Testing, and Inspection

FIELD EQUIPMENT	CALIBRATION ACTIVITY	MAINTENANCE ACTIVITY	TESTING ACTIVITY	INSPECTION ACTIVITY	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION	RESPONSIBLE PERSON	SOP REFERENCE[1]
Peristaltic Pump or equivalent	F-11	Per manufacturer's specifications		Check sample device	Daily	F-11	F-11	F-11	F-11
Water Level Meter	F-11	Per manufacturer's specifications	Water levels	Check sample device	Daily	F-11	F-11	F-11	F-11

[1] See Project Sampling SOP Reference table (Worksheet #21).

QAPP Worksheet #23
Analytical SOP References

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	DEFINITIVE OR SCREENING DATA	ANALYTICAL GROUP	INSTRUMENT	ORGANIZATION PERFORMING ANALYSIS	MODIFIED FOR PROJECT WORK? (Y/N)	ADDITIONAL EPA COMMENTS (BEYOND EXPIRATION DATE)?
W-1	Organochlorine and PCB (aroclor) pesticide analysis by GC/ECD, AM E-608, September 11, 2007	Definitive	Total PCB in water	Gas chromatography/ Electron capture detectors (GC/ECD)	Weyerhaeuser Analysis and Testing Services (WATS)	N	No – Approved by EPA with last version of Multi-Area QAPP
W-2	Suspended solids in water and wastewater. AM E-160.2, July 13, 2007	Definitive	TSS	Balance	WATS	N	No – Approved by EPA with last version of Multi-Area QAPP
W-3	Total and total soluble phosphorus in water, AM E-365.3, August 19, 2008	Definitive	Total phosphorus as P in water	Spectrophotometer	WATS	N	No – Approved by EPA with last version of Multi-Area QAPP
W-4	Polychlorinated biphenyl analysis by GC/ECD, AM E-8082, December 4, 2007	Definitive	Total PCB in soil and sediment	GC/ECD	WATS	N	No – Approved by EPA with last version of Multi-Area QAPP
W-5	Daily balance, water, and temperature checks, AQ-O-DLYCHK, February 21, 2007	Definitive	TSS	Balance	WATS	N	No – Approved by EPA with last version of Multi-Area QAPP
W-6	General Procedures for Performing Chromatographic Separations and Calibrations, AL G-8000, September 11, 2007	Definitive	General Procedures	Not Applicable	WATS	N	No – Approved by EPA with last version of Multi-Area QAPP
W-7	Sample Management Procedures, OP S-SMO, July 13, 2007	Definitive	Sample Management	Not Applicable	WATS	N	No – Approved by EPA with last version of Multi-Area QAPP
W-8	Procedure for Training Personnel to Perform Test Methods and Standard Operating Procedures. OQ TRAIN. August 19, 2008.	Not applicable	Training	Not Applicable	WATS	N	No – Approved by EPA with last version of Multi-Area QAPP
W-9	Analytical Procedure 3500, AC G-3500, August 15, 2008	Definitive	PCBs and SVOCs in water	Not Applicable	WATS	N	Yes – But revised by WATS 7/07, per comment 10.6 in 6/07 EPA Letter

QAPP Worksheet #23
Analytical SOP References

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	DEFINITIVE OR SCREENING DATA	ANALYTICAL GROUP	INSTRUMENT	ORGANIZATION PERFORMING ANALYSIS	MODIFIED FOR PROJECT WORK? (Y/N)	ADDITIONAL EPA COMMENTS (BEYOND EXPIRATION DATE)?
W-10	Extraction by Continuous Liquid-Liquid Extractor, AC G-3520, August 19, 2008	Definitive	VOCs, SVOCs, and PCBs in water(1)	Not Applicable	WATS	N	Yes – See Footnote (1) per Comment 10.8 in 6/07 EPA Letter.
W-11	Sonication for Soil and Sediments, AC G-3550, July 13, 2007	Definitive	PCBs and SVOCs in soil and sediment(2)	Not Applicable	WATS	N	Yes – See Footnote (2) per comment 10.7 in 6/07 EPA Letter
W-12	Acid Digestion of Aqueous Samples & Extracts for Metals Analysis by ICP & ICPMS, AM E-3010, March 6, 2007	Definitive	Metals in water	Not Applicable	WATS	N	No – Comment 12 in 6/07 EPA letter was suggestion only
W-13	Acid Digestion of Sediments, Soils, Sludges, and Other Solid Samples for Analysis by ICP & ICPMS, AM E-3050, March 6, 2007	Definitive	Metals in soil	Not Applicable	WATS	N	No - Comment 13 in 6/07 EPA letter was suggestion only
W-14	Metals Analysis by ICPMS. AM E-200.8M. August 15, 2008	Definitive	Metals in water and soil	Inductively Coupled Plasma Mass Spectrometer (ICPMS)	WATS	N	Yes – Replaced per Comment 16 in 6/07 EPA Letter
W-15	Capillary GC/MS for Semivolatile Organics. AM E-8270. July 20, 2007	Definitive	SVOCs in water and soil	GC/MS, capillary column	WATS	N	Yes – But revised by WATS 6/07, per comment 10.10 in 6/07 EPA Letter. Revised by WATS 6/09
W-16	Total Solids in Solid and Semi-Solid Samples. AM S-2540G. August 19, 2008.	Definitive	Total solids in soil and sediment	Scale	WATS	N	Added per U.S. EPA 6/07 Comments
W-17	Procedure for Florisil Clean Up of Organic Extracts. AC G-3620. September 11, 2007.	Definitive	PCBs in water, soil, and sediment	Not applicable	WATS	N	Added per U.S. EPA 6/07 Comments

QAPP Worksheet #23
Analytical SOP References

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	DEFINITIVE OR SCREENING DATA	ANALYTICAL GROUP	INSTRUMENT	ORGANIZATION PERFORMING ANALYSIS	MODIFIED FOR PROJECT WORK? (Y/N)	ADDITIONAL EPA COMMENTS (BEYOND EXPIRATION DATE)?
W-18	Gel Permeation Clean-Up. AP E-3640. August 19, 2008.	Definitive	PCBs and SVOCs in water, soil, and sediment	Not applicable	WATS	N	Added per U.S. EPA 6/07 Comments
W-19	Condensation and Evaporation Techniques. AC G-CONC. August 19, 2008.	Definitive	PCBs and SVOCs in water, soil, and sediment	Not applicable	WATS	N	Added per U.S. EPA 6/07 Comments
W-20	Organic Laboratory Analytical Standards. AC G-ORGSTD. July 18, 2007.	Definitive	VOCs, SVOCs, and PCBs in water, soil, and sediment	Not applicable	WATS	N	Added per U.S. EPA 6/07 Comments
W-21	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry, AM E-8260. August 27, 2008.	Definitive	VOCs in water	GC/MS	WATS	N	
W-22	Diesel and Motor Oil Range Compounds, Analysis of. AM U-WTPH-D. August 20, 2008.	Definitive	Diesel range compounds	GC/FID, Capillary column	WATS	N	
W-23	Gasoline Range Compounds, Analysis of. AM U-WTPH-G. August 19, 2008.	Definitive	Gasoline range compounds	GC/FID, megabore column	WATS	N	
W-24	Cyanide, Total, AM E-335.2 CLP-M. August 27, 2008	Definitive	Cyanide	Spectrophotometer	WATS	N	
W-25	Synthetic Precipitation Leaching Procedure (SPLP) AM E-1312, March 31, 2003	Defnitive	Metals in soil	Not applicable	WATS	N	
W-26	Hardness by Calculation, AM S-2340B, June 12, 2007	Defnitive	Hardness in water	Not applicable	WATS	N	
C-1	Sample Disposal, SMO-SDIS, Rev 7. March 26, 2008	Not Applicable	Sample Disposal	Not Applicable	Columbia Analytical Services (CAS)	N	

QAPP Worksheet #23
Analytical SOP References

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	DEFINITIVE OR SCREENING DATA	ANALYTICAL GROUP	INSTRUMENT	ORGANIZATION PERFORMING ANALYSIS	MODIFIED FOR PROJECT WORK? (Y/N)	ADDITIONAL EPA COMMENTS (BEYOND EXPIRATION DATE)?
C-2	Sample Tracking and Internal Chain-of-Custody, SMO-SCOC, Rev 12, April 23, 2009	Not Applicable	Chain-of-Custody	Not Applicable	CAS	N	
C-3	Sample Receiving, SMO-GEN, Rev 25, April 9, 2009	Not Applicable	Sample Receiving	Not Applicable	CAS	N	
C-4	Mercury in Water by Atomic Fluorescence Spectrometry, MET-1631, Rev 9. March 21, 2008	Definitive	Low-flow mercury in water	Cold-Vapor Atomic Fluorescence Spectrometer (CVAFS)	CAS	N	
C-5	Volatile Organic Compounds by GC/MS. VOC-8260, REV 12. March 21, 2008.	Definitive	VOCs in soil or water	GC/MS, Capillary column	CAS	N	
C-6	Purge and Trap/extraction for volatile organics in soil and waste samples, closed system. VOC-5035, REV 7. February 1, 2008.	Definitive	VOCs in soil and waste	Not applicable	CAS	N	
C-7	Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS Rev 0, MET-1630W, April 12, 2006	Definitive	Low Level Mercury in Water	Cold-Vapor Atomic Fluorescence Spectrometer (CVAFS)	CAS	N	
C-8	Nitrate/Nitrite, Nitrite By Flow Injection Analysis, GEN-353.2, Rev 6, January 5, 2006	Definitive	Nitrate/Nitrite in Soil	Flow injection Analyzer	CAS	N	
C-9	Ammonia By Flow Injection Analysis GEN-350.1, Rev 7, May 1, 2007	Definitive	Ammonia-N in Soil	Flow injection Analyzer	CAS	N	
C-10	Phosphorous Determination Using Colorimetric Procedure GEN-365.3, Rev 10, August 28, 2008	Definitive	Phosphorus in Soil	Spectrophotometer	CAS	N	

QAPP Worksheet #23
Analytical SOP References

REFERENCE NUMBER	TITLE, REVISION DATE, AND/OR NUMBER	DEFINITIVE OR SCREENING DATA	ANALYTICAL GROUP	INSTRUMENT	ORGANIZATION PERFORMING ANALYSIS	MODIFIED FOR PROJECT WORK? (Y/N)	ADDITIONAL EPA COMMENTS (BEYOND EXPIRATION DATE)?
C-11	Laboratory Balance Monitoring and Calibration, (ADM-BAL.1) August 7, 2008	Definitive	Various (Weighing samples, standards and reagents)	Balance	CAS	N	
C-12	Corrective Action (ADM-CA), Rev 5, September 12, 2007	Not Applicable	Corrective Action	Not Applicable	CAS	N	
S-1	Method 8082 for Polychlorinated Biphenyls (PCBs) by Gas Chromatography. SOP 8082, REV 4, May 21, 2007	Definitive	PCBs in oil	GC/ECD	Summit Environmental Testing (SET)	N	
S-2	ASTM Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids	Definitive	Free product/oil viscosity	Viscometer	SET	N	
S-3	ASTM Standard Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)	Definitive	Specific Gravity	Hydrometer	SET	N	

Notes:
(1) See appropriate analytical method for a discussion of how the extract will be stored if not immediately analyzed.
(2) Volumes of surrogates and matrix spiking are logged in the laboratory standard log book

QAPP Worksheet #24
Analytical Instrument Calibration

INSTRUMENT	CALIBRATION PROCEDURE	FREQUENCY OF CALIBRATION	ACCEPTANCE CRITERIA	CORRECTIVE ACTION (CA)	PERSON RESPONSIBLE FOR CA	SOP REFERENCE[1]
Cold-Vapor Atomic Fluorescence Spectrometer (CVAFS)	See C-4, C-7	At the beginning of each analysis sequence.	See C-4, C-7	Correct the problem and repeat the calibration.	Analyst	C-4, C-7
ICPMS	See W-14, W-26	At the beginning of each analysis sequence. CCV analyzed after calibration, after every 10 samples (max) and at end. Initial calibration blank/verification follow first CCV.	See W-14, W-26	Inspect the instrument, correct problems, repeat calibration.	Analyst	W-14, W-26
GC/MS	Tuning. See C-5, W-15 & W-21	Before 12 hr. sample analysis.	See C-5, W-15 & W-21	Inspect the instrument, correct problems, re-tune and/or recalibrate	Analyst	See C-5, W-15 & W-21
	Calibration, See C-5, W-15 & W-21	Initial calibration at instrument set-up and when calibration verification or tuning fail criteria. Calibration verification before 12 hr. sample analysis	See C-5, W-15 & W-21	Inspect the instrument, correct problems and recalibrate.	Analyst	See C-5, W-15 & W-21

QAPP Worksheet #24
Analytical Instrument Calibration

INSTRUMENT	CALIBRATION PROCEDURE	FREQUENCY OF CALIBRATION	ACCEPTANCE CRITERIA	CORRECTIVE ACTION (CA)	PERSON RESPONSIBLE FOR CA	SOP REFERENCE[1]
GC/FID	See W-22 & W-23	Initial calibration at instrument set-up and when calibration verification fails criteria. Check mid-point standards after every 10 samples and at the beginning and end of the analysis.	Initial calibration RSD ≤ 20% For continuing calibration standard must not exceed a percent difference of ± 15	Inspect system, correct problem, and rerun calibration on affected samples.	Analyst	See W-22 & W-23
GC/ECD	See W-1, W-4 & S-1	After initial calibration, a check standard of the match-point Aroclor 1016/1260 mixture is analyzed after every 10 samples and at the end of the sequence.	Initial calibration RSD for 1016/1260 ≤ 20% or linear regression >0.99 Continuing calibration standard must not exceed a percent difference of ± 15	Inspect system, correct problem, and rerun calibration on affected samples.	Analyst	See W-1, W-4 & S-1
Balance	See SOP W-5.	Daily	NA	Inspect system, correct problem, and rerun calibration on affected samples.	Analyst	W-2 and W-5

QAPP Worksheet #24
Analytical Instrument Calibration

INSTRUMENT	CALIBRATION PROCEDURE	FREQUENCY OF CALIBRATION	ACCEPTANCE CRITERIA	CORRECTIVE ACTION (CA)	PERSON RESPONSIBLE FOR CA	SOP REFERENCE[1]
Flow Injection Analyzer	See SOP C-8, C-9	Initial calibration at instrument set-up and when calibration verification fails criteria. Verification checked with blank and three standards at the beginning of the analysis. Analyze continuing calibration standard after every 10 samples and at end of sequence.	See SOP C-8 and C-9	Inspect system, correct problem, and rerun calibration on affected samples.	Analyst	C-8, C-9
Spectrophotometer	Construct two 6-point calibration curves of absorbance versus concentration for low and high levels (one curve for Phosphorus).	Before sample analysis, when check standard is outside Confidence Limits; also, after major instrument maintenance	See SOPs W-3, W-24, C-10	Fix problem and recalibrate.	Analyst	W-3, W-24, C-10
Hydrometer	Known Standard	Weekly	± 10% of Standard	See S-2	Analyst	S-2
Viscometer	Known Standard	Weekly	± 10% of Standard	See S-3	Analyst	S-3

Footnote:
(1) See Analytical SOP References (Worksheet #23).

QAPP Worksheet #25
Analytical Instrument and Equipment Maintenance, Testing, and Inspection

INSTRUMENT/ EQUIPMENT	MAINTENANCE ACTIVITY	TESTING ACTIVITY	INSPECTION ACTIVITY	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION	RESPONSIBLE PERSON	SOP REFERENCE[1]
GC/ECD	▪ Change septa weekly, or as needed. ▪ Change gas line dryers as needed. ▪ Replace injection port liner weekly, or as needed. ▪ Clip column. ▪ Replace GC column as needed. ▪ Clean/Replace detector as needed. ▪ Provide that gas supply is sufficient and delivery pressure is adequate.	Conduct leak test.	Check connections and bake out instrument.	W-1 and W-4	W-1 and W-4	Inspect system, correct problem, rerun calibration, and reanalyze affected samples.	Analyst	W-1 and W-4
GC/MS	▪ See W-15, W-21, C-5		See W-15, W-21, C-5	See W-15, W-21, C-5	See W-15, W-21, C-5	Inspect system, correct problem, and rerun calibration on affected samples.	Analyst	See W-15, W-21, C-5
GC/FID	▪ See W-22, W-23		See W-22, W-23	See W-22, W-23	See W-22, W-23	Inspect system, correct problem, and rerun calibration on affected samples.	Analyst	See W-22, W-23
Spectro-photometer	▪ Dust lamp and front of front lens. ▪ Clean sample compartment. ▪ Clean windows. ▪ Clean cuvettes.		Check the zero.	Daily	See W-3, W-24, C-10	Inspect system, correct problem, and rerun calibration on affected samples.	Analyst	W-3, W-24, C-10
Flow Injection Analyzer	See C-8 and C-9		See C-8 and C-9	See C-8 and C-9	See C-8 and C-9	Inspect system, correct problems, re-run calibration and affected samples if necessary	Analyst	C-8 and C-9
Balance	▪ Professional service contract		NA	Once/year	NA	NA	Service contractor	NA

QAPP Worksheet #25
Analytical Instrument and Equipment Maintenance, Testing, and Inspection

INSTRUMENT/ EQUIPMENT	MAINTENANCE ACTIVITY	TESTING ACTIVITY	INSPECTION ACTIVITY	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION	RESPONSIBLE PERSON	SOP REFERENCE[1]
ICPMS	See ICPMS Instruction Manual		Check gas cylinder pressures, recirculator is 20°C, allow 30-min warm-up after ignition, run performance report, tune instrument.	W-14, W-26	W-14, W-26	Inspect system, resolve any deficiencies, rerun calibration on affected samples	Analyst	W-14, W-26
Cold-Vapor Atomic Fluorescence Spectrometer (CVAFS)	See C-4, C-7		See C-4, C-7	See C-4, C-7	See C-4, C-7	Inspect system, correct problems, re-run calibration and affected samples if necessary	Analyst	C-4, C-7
Hydrometer	Clean hydrometer and cylinder with mineral spirits after each use		Check for damaged hydrometer	S-2	See S-2	Reanalyze sample	Analyst	S-2
Viscometer	Clean viscosity tube with mineral spirits after each use.		Check for damage or capillary blockage	S-3	See S-3	Reanalyze sample	Analyst	S-3

Footnote:
[1] See Analytical SOP References (Worksheet #23).

QAPP Worksheet #26
Sample Handling System (WATS)

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (personnel/organization): Emily Stahl, CRA
Sample Packaging (personnel/organization): Emily Stahl, CRA
Coordination of Shipment (personnel/organization): Emily Stahl, CRA
Type of Shipment/Carrier: Overnight courier
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (personnel/organization): Dennis Catalano, WATS (or designee)
Sample Custody and Storage (personnel/organization): Dennis Catalano, WATS (or designee)
Sample Preparation (personnel/organization): Dennis Catalano, WATS (or designee)
Sample Determinative Analysis (personnel/organization): Dennis Catalano, WATS (or designee)
SAMPLE ARCHIVING
Field Sample Storage (number of days from sample collection): 30 days from submittal of final report
Sample Extract/Digestate Storage (number of days from extraction/digestion): 60 days from submittal of final report
Biological Sample Storage (number of days from sample collection): NA
SAMPLE DISPOSAL
Personnel/Organization: Dennis Catalano, WATS
Number of Days from Analysis: 60 days minimum from submittal of final report

QAPP Worksheet #27
Sample Custody Requirements

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory):

The field sampler is personally responsible for the care and custody of the samples until they are transferred to the laboratory or properly dispatched. Keeps the number of people handling the samples to a minimum to ensure proper field Chain-of-Custody.

Field Chain-of-Custody Records will accompany all analytical samples and sample shipping containers to document their transfer from the field to the analytical laboratory. The procedures to be implemented are as follows:

Complete CRA supplied Chain-of-Custody Records Indicating sample identification, containers filled, sampling date, sampling time, sample collector's name, and sample preservation, if applicable. Also note this information in the field notebooks.

Repack shipping containers with samples, Chain-of-Custody Records, and water ice. Assign a Chain-of-Custody Record to each set of sample containers to be shipped.

Place completed Chain-of-Custody Records in a plastic bag, seal the bag, and tape it to the inside cover of the shipping container. After the samples are iced, add the date to the Chain-of-Custody Record, seal the coolers with strapping tape, add custody seals, and ship the coolers to WATS Laboratory using an overnight delivery service. Identify common carriers or intermediate individuals on the Chain-of-Custody Record, and retain copies of all bills-of-lading. When the samples are received in the laboratory, handle and process them in accordance with laboratory SOPs, or specified analytical methods, as defined in this QAPP.

The laboratory receiving the samples will check shipping containers for completeness of paperwork, broken custody seals, damaged sample containers, and sample preservation as specified by the analytical method. The laboratory's sample management staff will note any problems, log the samples into the laboratory, and complete the Chain-of-Custody Record. The person relinquishing the samples to the facility or agency will request the representative's signature acknowledging sample receipt. If the representative is unavailable or refuses, this is to be noted in the "Received By" space on the Record.

Include copies of the Chain-of-Custody Record with the analytical data.

A separate sample receipt is prepared whenever samples are split with a government agency. The receipt is marked to indicate with whom the samples are being split. The person relinquishing the samples to the agency should request the agency representative's signature acknowledging sample receipt. If the representative is unavailable or refuses, this is to be noted on the receipt and in the field notebook.

A copy of the Chain-of-Custody Record will accompany the samples to the laboratory. The field sampling personnel will retain one copy with the field notes. If a Chain-of-Custody Record Is damaged in shipment, the field copy will be made available. A written statement will be prepared by the person who collected the samples, listing the samples that were recorded on the damaged record, and describing when and how the samples were collected. The statement should include information such as field notebook entries regarding the sample. This statement is submitted to Field QA Officer and the CRA Project Manager for further action, as necessary.

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal):

The laboratory assigns a unique, sequentially numbered sample code to each sample received. Laboratory custody procedures for sample receiving and log-in, storage, tracking, and holding time requirements are described in the laboratory's Quality Assurance Manual and in the Laboratory SOPs (see Attachment 1-5).

QAPP Worksheet #27 (*continued*)
Sample Custody Requirements

Sample Identification Procedures:

Label each bottle with the project number, the sample identifier, the sample type, the sampler's initials, and the date and time of sample collection.

Complete sample labels for each sample and custody seals for each shipment container using waterproof ink, unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample tag because the ink pen would not function in freezing weather.

Chain-of-Custody Procedures:

An example Chain-of-Custody Record from WATS Laboratory is shown in Attachment 1-3. The Records should be legibly completed. Errors will be corrected by drawing a single line through the incorrect information and entering the correct information. All corrections are to be initialed and dated by the person making the correction. This procedure applies to words or figures inserted or added to a previously recorded statement.

The following information must be included on the Chain-of-Custody Record Attachment 1-3:

Facility name and address, project number, and sampler identification.

"The Sample ID No. and Description" portion of the Record must be completed for each sample. This information includes the Field Sample ID, sample date and time, and sample depth. The sampling time **MUST** also be noted on the sample bottle (except for blind field duplicates, where date and time would <u>not</u> be noted on the bottle label or Chain-of-Custody Record).

The sample container type and number, sample matrix, preservative/filtration, and requested analysis must be designated by checking the appropriate box and/or writing the required information.

Sample custody is documented on the lower portion of the Record, and includes the sampler's signature, signatures of persons involved in the possession of the sample with dates and times, and the date on which the sample was received at the laboratory, as described further below.

Relinquished by/Received by - This part of the Chain-of-Custody Record is a record of the individuals who actually had the samples in their custody. The spaces must be used in chronological order as the Chain-of-Custody Record is transferred with the samples.

(1) Sampler signs when relinquishing custody.
(1) Person accepting custody of samples from sampler signs.
(2) Person in (1) must sign when relinquishing custody.
(2)-(3) These are completed as necessary in the same manner as above.

Sampler - The person/persons collecting the samples must <u>sign</u> their name and <u>print</u> their name under their signature, and record the date and time they relinquish the samples to either the laboratory or the shipper. The final signature is that of the person receiving the samples at the laboratory.

Special Instructions – The sampler may provide additional information about a sample, *e.g.*, if an odor is present, high or low pH, etc.

Possible Hazard Identification – The sampler may include any known <u>or</u> suspected hazards associated with the samples. Sample entry personnel may add information to this section based on communications from the laboratory Project Manager or Supervisor after samples are received. Laboratory Team Leaders will use any hazard information to update and advise their analysts before work is started.

<u>**Note**</u>**:** If commercial carriers are used, the name of the carrier, any airbill number, and the date and time of relinquishing the sample containers are written on the airbill by sample entry or field personnel, and the airbill is attached to the Chain-of-Custody Record.

A copy of the Chain-of-Custody Record should be returned with the sample results. The laboratory service request number should be written on the Chain-of-Custody Record to facilitate its use during project data entry.

QAPP Worksheet #28-1
QC Samples - PCBs (Surface Water/Groundwater)

Matrix: Water
Sampling SOP: F-11, F-16
Field Sampling Organization: CRA
Analytical Group: PCBs
Analytical Method/SOP Reference: W-1
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <20	Qualify data as needed.	CRA QA Officer	Precision	RPD
Surrogates	2 per sample	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-2
QC Samples - TSS (Surface Water)

Matrix: Water
Sampling SOP: F-16
Field Sampling Organization: CRA
Analytical Group: TSS
Analytical Method/SOP Reference: W-2, W5
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18[1]

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <20	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery

QAPP Worksheet #28-3
QC Samples - Phosphorus (Surface Water)

Matrix: Water
Sampling SOP: F-16
Field Sampling Organization: CRA
Analytical Group: Total phosphorus
Analytical Method/SOP Reference: W-3
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <20	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-4
QC Samples - PCBs (Soil/Sediment)

Matrix: Soil/Sediment
Sampling SOP: F-4, F-5, F-6
Field Sampling Organization: CRA
Analytical Group: PCBs
Analytical Method/SOP Reference: W-4
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <50	Qualify data as needed.	CRA QA Officer	Precision	RPD
Surrogates	2 per sample	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-5
QC Samples - PCBs (Free Product)

Matrix: Free Product
Sampling SOP: F-1, F-3
Field Sampling Organization: CRA
Analytical Group: PCBs
Analytical Method/SOP Reference: S-1
Analytical Organization: SET
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18[1]

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <100	Qualify data as needed.	CRA QA Officer	Precision	RPD
Surrogates	1 per sample	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-6
QC Samples –Metals (Groundwater)

Matrix: Water
Sampling SOP: F-11
Field Sampling Organization: CRA
Analytical Group: Metals
Analytical Method/SOP Reference: W-14
Analytical Organization: WATS
Concentration Level: All (Except Low-Level Mercury)
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-digestion/ reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-7
QC Samples –Metals (Soil/SPLP)

Matrix: Soil
Sampling SOP: F-5, F-6
Field Sampling Organization: CRA
Analytical Group: Metals and SPLP Metals
Analytical Method/SOP Reference: W-14
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-digestion/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-8
QC Samples – Cyanide (Groundwater)

Matrix: Water
Sampling SOP: F-11
Field Sampling Organization: CRA
Analytical Group: Cyanide
Analytical Method/SOP Reference: W-24
Analytical Organization: WATS
Concentration Level: Total
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-digestion/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-9
QC Samples – Cyanide (Soil)

Matrix: Soil
Sampling SOP: F-5, F-6
Field Sampling Organization: CRA
Analytical Group: Cyanide
Analytical Method/SOP Reference: W-24
Analytical Organization: WATS
Concentration Level: Total
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-digestion/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-10
QC Samples – Low Level Mercury (Surface Water/Groundwater)

Matrix: Water
Sampling SOP: F-11, F-16
Field Sampling Organization: CRA
Analytical Group: Mercury
Analytical Method/SOP Reference: C-4
Analytical Organization: CAS
Concentration Level: Low-Level
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-digestion/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Trip blanks	1 per cooler	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-11
QC Samples - SVOCs (Groundwater)

Matrix: Water
Sampling SOP: F-11
Field Sampling Organization: CRA
Analytical Group: SVOCs
Analytical Method/SOP Reference: W-15
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	6 per sample	Laboratory control limits	Re-extraction/ Re-analysis	Laboratory Staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-12
QC Samples - SVOCs (Soil)

Matrix: Soil
Sampling SOP: F-5, F-6
Field Sampling Organization: CRA
Analytical Group: SVOCs
Analytical Method/SOP Reference: W-15
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	6 per sample	Laboratory control limits	Re-extraction/ Re-analysis	Laboratory Staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-13
QC Samples - VOCs (Groundwater)

Matrix: Water
Sampling SOP: F-11
Field Sampling Organization: CRA
Analytical Group: VOCs
Analytical Method/SOP Reference: W-21
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	3 per sample	Laboratory control limits	Re-analysis	Laboratory Staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Trip blank	1 per cooler	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA Data Validator	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-14
QC Samples - VOCs (Soil)

Matrix: Soil
Sampling SOP: F-5, F-6
Field Sampling Organization: CRA
Analytical Group: VOCs
Analytical Method/SOP Reference: C-5
Analytical Organization: CAS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	4 per sample	Laboratory control limits	Re-analysis	Laboratory Staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-15
QC Samples – DRO & GRO (Soil)

Matrix: Soil
Sampling SOP: F-5, F-6
Field Sampling Organization: CRA
Analytical Group: DRO & GRO
Analytical Method/SOP Reference: W-22& W-23
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 100%	Qualify data as needed	CRA QA Officer	Precision	RPD
Surrogates	1 per sample (DRO) 2 per sample (GRO)	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory Staff	Accuracy	% Recovery
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory Control Sample (LCS)	1 per analytical batch	Laboratory control limits	Reanalysis	Laboratory Staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-16
QC Samples - Hardness (Surface Water)

Matrix: Water
Sampling SOP: F-16
Field Sampling Organization: CRA
Analytical Group: Hardness (Calculation)
Analytical Method/SOP Reference: W-26
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <50	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-17
QC Samples – Methyl Mercury (Surface Water/Groundwater)

Matrix: Water
Sampling SOP: F-16, F-11
Field Sampling Organization: CRA
Analytical Group: Methyl Mercury
Analytical Method/SOP Reference: C-7
Analytical Organization: WATS
Concentration Level: Low-Level
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per ten samples	RPD < 50%	Qualify data as needed	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-digestion/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per ten samples	< Laboratory reporting limit	Qualify data as needed	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-digestion/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-18
QC Samples - Phosphorus (Soil)

Matrix: Soil
Sampling SOP: F-5, F-6
Field Sampling Organization: CRA
Analytical Group: Total phosphorus (Wet Chemistry)
Analytical Method/SOP Reference: C-10
Analytical Organization: CAS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <100	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-19
QC Samples – Ammonia-N (Soil)

Matrix: Soil
Sampling SOP: F-5, F-6
Field Sampling Organization: CRA
Analytical Group: Ammonia-N (Wet Chemistry)
Analytical Method/SOP Reference: C-9
Analytical Organization: CAS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <100	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-20
QC Samples – Nitrate-N (Soil)

Matrix: Soil
Sampling SOP: F-5, F-6
Field Sampling Organization: CRA
Analytical Group: Nitrate-N (Wet Chemistry)
Analytical Method/SOP Reference: C-8
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <100	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #28-21
QC Samples – Nitrite-N (Soil)

Matrix: Soil
Sampling SOP: F-5, F-6
Field Sampling Organization: CRA
Analytical Group: Nitrite-N (Wet Chemistry)
Analytical Method/SOP Reference: C-8
Analytical Organization: WATS
Concentration Level: All
Sampler's Name: NA
Number of Sample Locations: As identified in appropriate WS 18

QC SAMPLE	FREQUENCY/ NUMBER	METHOD/SOP QC ACCEPTANCE LIMITS	CORRECTIVE ACTION	PERSON(S) RESPONSIBLE FOR CORRECTIVE ACTION	DATA QUALITY INDICATOR (DQI)	MEASUREMENT PERFORMANCE CRITERIA
Field duplicate	1 per 10 samples	RPD <100	Qualify data as needed.	CRA QA Officer	Precision	RPD
Method blanks	1 per analytical batch	< Laboratory reporting limit	Re-extraction/ Reanalysis	Laboratory staff	Bias/Contamination	< Laboratory reporting limit
Equipment blanks	1 per 10 samples	< Laboratory reporting limit	Qualify data as needed.	CRA QA Officer	Bias/Contamination	< Laboratory reporting limit
Laboratory control sample (LCS)	1 per analytical batch	Laboratory control limits	Re-extraction/ Reanalysis	Laboratory staff	Accuracy	% Recovery
MS/MSD	1 per 20 samples	Laboratory control limits	Qualify data as needed.	Laboratory staff CRA QA Officer	Accuracy/Precision	% Recovery/RPD

QAPP Worksheet #30
Analytical Services

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	SAMPLE LOCATIONS/ ID NUMBERS	ANALYTICAL SOP	DATA PACKAGE TURNAROUND TIME	LABORATORY/ ORGANIZATION (name, address, contact person, and telephone number)	BACKUP LABORATORY/ ORGANIZATION (name, address, contact person, and telephone number)
Ground/ Surface water	PCBs, TSS, Phosphorus, Metals/SPLP metals, Total Cyanide, SVOCs, VOCs, Hardness	All	TBD	W-1, W-2, W-5 W-3, W-14, W-24 W-15 W-21, W-26	Standard turnaround time (21 calendar days)	Weyerhaeuser Analysis and Testing Services (WATS) Weyerhaeuser Company Mail Stop: WTC2F25 32901 Weyerhaeuser Way Federal Way, WA 98001 Dennis Catalano 253.924.6242	TestAmerica, Laboratories, Inc. 4101 Shuffel Street NW North Canton, OH 44720 Denise Heckler (800) 456-9396
	Mercury (low level) Methyl Mercury	All	TBD	C-4 C-7	Standard turnaround time (21 calendar days)	Columbia Analytical Services (CAS), Inc 1317 South 13th Avenue Kelso, WA 98626 Jeff Christian 360.557.7222	TestAmerica, Laboratories, Inc. 4101 Shuffel Street NW North Canton, OH 44720 Denise Heckler (800) 456-9396
Free Product	Specific Gravity, Viscosity, PCBs	All	TBD	S-1, S-2, S-3	Standard turnaround time (2 calendar days)	Summit Environmental Technologies, Inc (SET) Analytical Laboratories 3310 Win Street Cuyhoga Falls, OH 44223 Ron Gibas 800.278.0140	TestAmerica, Laboratories, Inc. 4101 Shuffel Street NW North Canton, OH 44720 Denise Heckler (800) 456-9396

QAPP Worksheet #30
Analytical Services

MATRIX	ANALYTICAL GROUP	CONCENTRATION LEVEL	SAMPLE LOCATIONS/ ID NUMBERS	ANALYTICAL SOP	DATA PACKAGE TURNAROUND TIME	LABORATORY/ ORGANIZATION (name, address, contact person, and telephone number)	BACKUP LABORATORY/ ORGANIZATION (name, address, contact person, and telephone number)
Soil/ Sediment	PCBs, Metals, SVOCs, DRO/GRO, Cyanide Phosphorous, Ammonia-N Nitrate-N Nitrite-N	All	TBD	W-4, W-14, W-15, W-22/W-23 W-25 C-10 C-9 C-8 C-8	Standard turnaround time (21 calendar days)	Weyerhaeuser Analysis and Testing Services (WATS) Weyerhaeuser Company Mail Stop: WTC2F25 32901 Weyerhaeuser Way Federal Way, WA 9800 Dennis Catalano 253.924.6242	TestAmerica, Laboratories, Inc. 4101 Shuffel Street NW North Canton, OH 44720 Denise Heckler (800) 456-9396
	VOCs	All	TBD	C-5, C-6	Standard turnaround time (21 calendar days)	Columbia Analytical Services (CAS), Inc 1317 South 13th Avenue Kelso, WA 98626 Jeff Christian 360.557.7222	TestAmerica, Laboratories, Inc. 4101 Shuffel Street NW North Canton, OH 44720 Denise Heckler (800) 456-9396
Independent Data Validation	All	All	--	All	--	Conestoga Rovers & Associates 14496 Sheldon Rd Suite 200 Plymouth, MI 48170 Paul Wiseman 734.453.5123	--

Notes:
NA = not applicable.
TBD = to be determined.

QAPP Worksheet #31-4
Planned Project Assessments
Plainwell Mill Phase II RI Work Plan

ASSESSMENT TYPE	FREQUENCY	INTERNAL OR EXTERNAL	ORGANIZATION PERFORMING ASSESSMENT	PERSON(S) RESPONSIBLE FOR PERFORMING ASSESSMENT (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR RESPONDING TO ASSESSMENT FINDINGS (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR IDENTIFYING AND IMPLEMENTING CORRECTIVE ACTIONS (CA) (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR MONITORING EFFECTIVENESS OF CA (title and organizational affiliation)
Field performance audit	Periodic, based on field schedule	Internal	CRA	Gregory Carli, CRA (Project Manager)	Emily Stahl, CRA (Project Coordinator)	Golnoush Bolourani, CRA (Field QA Officer)	Emily Stahl, CRA (Project Coordinator)
Field systems audit	Periodic, based on field schedule	Internal	CRA	Paul Wiseman CRA (QA Officer)	Emily Stahl, CRA (Project Coordinator)	Golnoush Bolourani, CRA (Field QA Officer)	Emily Stahl, CRA (Project Coordinator)
Laboratory audit	As needed, based on laboratory performance	Internal	CRA	Paul Wiseman CRA (QA Officer)	Dennis Catalano, WATS (Laboratory Manager)	Dennis Catalano, WATS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)
Laboratory audit	Per laboratory QA Plan	Internal	WATS	Dennis Catalano, WATS (Laboratory Manager)	Dennis Catalano, WATS (Laboratory Manager)	Dennis Catalano, WATS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)

QAPP Worksheet #31-5
Planned Project Assessments
12th Street Landfill RA Work Plan

ASSESSMENT TYPE	FREQUENCY	INTERNAL OR EXTERNAL	ORGANIZATION PERFORMING ASSESSMENT	PERSON(S) RESPONSIBLE FOR PERFORMING ASSESSMENT (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR RESPONDING TO ASSESSMENT FINDINGS (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR IDENTIFYING AND IMPLEMENTING CORRECTIVE ACTIONS (CA) (title and organizational affiliation)	PERSON(S) RESPONSIBLE FOR MONITORING EFFECTIVENESS OF CA (title and organizational affiliation)
Field performance audit	Periodic, based on field schedule	Internal	CRA	Gregory Carli, CRA (Project Manager)	Jodie Dembowske, CRA (Project Coordinator)	Golnoush Bolourani, CRA (Field QA Officer), and Wayne Bauman, CRA (Construction Manager)	Jodie Dembowske, CRA (Project Coordinator)
Field systems audit	Periodic, based on field schedule	Internal	CRA	Paul Wiseman CRA (QA Officer)	Jodie Dembowske, CRA (Project Coordinator)	Golnoush Bolourani, CRA (Field QA Officer), and Wayne Bauman, CRA (Construction Manager)	Jodie Dembowske, CRA (Project Coordinator)
Laboratory audit	As needed, based on laboratory performance	Internal	CRA	Paul Wiseman CRA (QA Officer)	Dennis Catalano, WATS (Laboratory Manager)	Dennis Catalano, WATS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)
Laboratory audit	Per laboratory QA Plan	Internal	WATS	Dennis Catalano, WATS (Laboratory Manager)	Dennis Catalano, WATS (Laboratory Manager)	Dennis Catalano, WATS (Laboratory Manager)	Paul Wiseman CRA (QA Officer)

QAPP Worksheet #32-3
Assessment Findings and Corrective Action Responses
Plainwell Mill Phase II RI Work Plan

ASSESSMENT TYPE	NATURE OF DEFICIENCIES DOCUMENTATION	INDIVIDUAL(S) NOTIFIED OF FINDINGS (name, title, organization)	TIME FRAME OF NOTIFICATION	NATURE OF CORRECTIVE ACTION RESPONSE DOCUMENTATION	INDIVIDUAL(S) RECEIVING CORRECTIVE ACTION RESPONSE (name, title, organization)	TIME FRAME FOR RESPONSE
Field performance audit	Checklist	Emily Stahl, CRA (Project Coordinator), will notify Gregory Carli, CRA (Project Manager).	Within 72 hours after audit (or sooner, as appropriate)	E-mail response	Golnoush Bolourani, CRA (Field QA Officer)	Within 48 hours after notification (or sooner, as appropriate)
Field systems audit	Checklist	Paul Wiseman, CRA (QA Officer), will notify Gregory Carli, CRA (Project Manager).	Within 48 hours after audit (or sooner, as appropriate)	E-mail response	Golnoush Bolourani, CRA (Field QA Officer)	Within 48 hours after notification (or sooner, as appropriate)
Internal laboratory audit	Executive Summary from Management Report	Dennis Catalano, WATS (Laboratory Manager), will notify Paul Wiseman, CRA (QA Officer), and appropriate laboratory staff.	Within 48 hours after audit (or sooner, as appropriate)	Executive Summary from Management Report	Paul Wiseman, CRA (QA Officer), and appropriate laboratory staff	Within 48 hours after notification (or sooner, as appropriate)
External laboratory audit	Checklist	Paul Wiseman, CRA (QA Officer), will notify Dennis Catalano, WATS (Laboratory Manager), and Gregory Carli (Project Manager).	Within 1 week after audit	Memorandum	Dennis Catalano, WATS (Laboratory Manager)	Within 48 hours after notification (or sooner, as appropriate)

QAPP Worksheet #32-4
Assessment Findings and Corrective Action Responses
Plainwell Mill Phase II RI Work Plan

ASSESSMENT TYPE	NATURE OF DEFICIENCIES DOCUMENTATION	INDIVIDUAL(S) NOTIFIED OF FINDINGS (name, title, organization)	TIME FRAME OF NOTIFICATION	NATURE OF CORRECTIVE ACTION RESPONSE DOCUMENTATION	INDIVIDUAL(S) RECEIVING CORRECTIVE ACTION RESPONSE (name, title, organization)	TIME FRAME FOR RESPONSE
Field performance audit	Checklist	Jodie Dembowske, CRA (Project Director), will notify Gregory Carli, CRA (Project Manager).	Within 72 hours after audit (or sooner, as appropriate)	E-mail response	Golnoush Bolourani, CRA (Field QA Officer), and Wayne Bauman, CRA (Construction Manager)	Within 48 hours after notification (or sooner, as appropriate)
Field systems audit	Checklist	Paul Wiseman, CRA (QA Officer), will notify Gregory Carli, CRA (Project Manager).	Within 48 hours after audit (or sooner, as appropriate)	E-mail response	Golnoush Bolourani, CRA (Field QA Officer), and Wayne Bauman, CRA (Construction Manager)	Within 48 hours after notification (or sooner, as appropriate)
Internal laboratory audit	Executive Summary from Management Report	Dennis Catalano, WATS (Laboratory Manager), will notify Paul Wiseman, CRA (QA Officer), and appropriate laboratory staff.	Within 48 hours after audit (or sooner, as appropriate)	Executive Summary from Management Report	Paul Wiseman, CRA (QA Officer), and appropriate laboratory staff	Within 48 hours after notification (or sooner, as appropriate)
External laboratory audit	Checklist	Paul Wiseman, CRA (QA Officer), will notify Dennis Catalano, WATS (Laboratory Manager), and Gregory Carli (Project Manager).	Within 1 week after audit	Memorandum	Dennis Catalano, WATS (Laboratory Manager)	Within 48 hours after notification (or sooner, as appropriate)

QAPP Worksheet #33
QA Management Reports

TYPE OF REPORT	FREQUENCY (daily, weekly, monthly, quarterly, annually, etc.)	PROJECTED DELIVERY DATE(S)	PERSON(S) RESPONSIBLE FOR REPORT PREPARATION (title and organizational affiliation)	REPORT RECIPIENT(S) (title and organizational affiliation)
Field audit reports	As needed	As generated	Gregory Carli, CRA (Project Manager) Paul Wiseman, CRA (QA Officer)	Richard Gay (Weyerhaeuser Environmrtal Manager) Glenn Turchn (CRA Project Director)
WATS audit (external)	As needed	As generated	Paul Wiseman, CRA (QA Officer)	Richard Gay (Weyerhaeuser Environmrtal Manager) Glenn Turchan (CRA Project Director) Gregory Carl (Project Manager)
Data validation reports	As specified in data assessment section	As generated	Paul Wiseman, CRA (QA Officer)	Richard Gay (Weyerhaeuser Environmrtal Manager) Glenn Turchan (CRA Project Director) Gregory Carli (Project Manager)
Data quality summary	As appropriate for data use	As generated	Paul Wiseman, CRA (QA Officer)	Richard Gay (Weyerhaeuser Environmrtal Manager) Glenn Turchan (CRA Project Director) Gregory Carl (Project Manager)

QAPP Worksheet #34
Verification (Step I) Process

VERIFICATION INPUT	DESCRIPTION	INTERNAL/ EXTERNAL	RESPONSIBLE FOR VERIFICATION (name, organization)
Chain-of-Custody Records and shipping documentation	Chain-of-Custody Records and shipping documentation will be reviewed by the laboratory upon receipt of samples for verification against the sample coolers they represent. The Chain-of-Custody Record will be signed by all parties who had custody of samples, with the exception of commercial carriers.	Internal	Dennis Catalano, WATS (or designee) (Laboratory Manager)
Field notes and sampling logs	All field notes and sampling logs will be reviewed internally and placed in the project file.	Internal	Emily Stahl, CRA (Project Coordinator)
Laboratory data	All laboratory data packages will be verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal.	Internal	Dennis Catalano, WATS (or designee) (Laboratory Manager)
Laboratory data	All final data packages will be verified for content upon receipt.	Internal	Paul Wiseman, CRA (QA Officer)

QAPP Worksheet #35
Validation (Step I) Process

STEP IIa/IIb	VALIDATION INPUT	DESCRIPTION	RESPONSIBLE FOR VERIFICATION (Name, Organization)
Step IIa	Sampling methods and procedures	Verify that the required analytical methods were used and that any deviations were noted.	Paul Wiseman, CRA
Step IIa	Analytical methods	Verify that the required sampling methods were used and that any deviations were noted. The laboratory will verify that QC samples met the performance criteria, and that any deviations were noted on the sample narrative.	Dennis Catalano, WATS Paul Wiseman, CRA
Step IIb	Documentation of QAPP QC sample results	Establish that all QC samples required by the QAPP were collected and analyzed.	Paul Wiseman, CRA
Step IIb	Project Quantitation Limits	Determine that the QAPP-required Quantitation Limits were achieved.	Paul Wiseman, CRA
Step IIb	Validation report	Summarize data findings of verification and validation components included in the QAPP. Include comments on any qualified data, and define all qualifiers.	Paul Wiseman, CRA

QAPP Worksheet #36
Validation (Steps IIa and IIb) Summary

STEPS IIa AND IIb	MATRIX	ANALYTICAL GROUP	DATA PURPOSE	CONCENTRATION LEVEL	VALIDATION CRITERIA	DATA VALIDATOR (title and organizational affiliation)
IIa and IIb	Aqueous/ Soil/ Sediment	PCBs, VOCs, PAHs/SVOCs	Site Investigation, Remedial Design, or Confirmation of Remediation, Remedial Investigation, Remedial Action	Low, medium, high	U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (October 1999), method criteria, QAPP criteria; and professional judgment	Paul Wiseman (CRA)
IIa and IIb	Aqueous/ Soil/ Sediment	Metals, Cyanide, Low Level Mercury, Methyl Mercury	Site Investigation, Remedial Design, or Confirmation of Remediation, Remedial Investigation, Remedial Action	Low, medium, high	U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (October 2004, February 1994), method criteria, QAPP criteria; and professional judgment	Paul Wiseman (CRA)
IIa and IIb	Water	PCBs, VOCs, PAHs/SVOCs	Site Investigation, Remedial Design, Confirmation of Remediation, Remedial Investigation, Remedial Action, or Long Term Monitoring	Low, medium, high	U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (October 1999), method criteria, QAPP criteria; and professional judgment	Paul Wiseman (CRA)
IIa and IIb	Water	Metals, Cyanide, Low Level Mercury, Methyl Mercury	Site Investigation, Remedial Design, Confirmation of Remediation, Remedial Investigation, Remedial Action, or Long Term Monitoring	Low, medium, high	U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (October 2004, February 1994), method criteria, QAPP criteria; and professional judgment	Paul Wiseman (CRA)
IIa and IIb	Oil	PCBs, Specific Gravity, & Viscosity	Site Investigation, Remedial Action	Low, medium, high	U.S. EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (October 1999), method criteria, QAPP criteria; and professional judgment	Paul Wiseman (CRA)
IIa and IIb	Aqueous/ Soil/ Sediment	General chemistry parameters	Confirmation of remediation, Remedial Investigation, Remedial Action	Low, medium, high	U.S. EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (February 1994), method criteria, QAPP criteria; and professional judgment	Paul Wiseman (CRA)

QAPP Worksheet #37
Usability Assessment

Identify the personnel responsible for performing the usability assessment:

Conestoga Rovers & Associates (CRA), will perform the usability assessment for analytical data. Paul Wiseman is responsible for data validation at CRA. The CRA Project Coordinator is responsible for verification of field activities.

The CRA Project Manager, CRA Project Coordinator, and CRA QA Officer will determine if field and analytical data or datasets meet the requirements necessary for decision-making. The results of these measurements will be compared with the DQO requirements set forth in this QAPP. As data are evaluated, anomalies in the data or data gaps may become apparent to the data users. The DQOs will be satisfied if the data are sufficient (based on the quality and completeness of the data) to meet the project objectives.

Data that do not meet the data users' needs (if any) will be identified and appropriately qualified in the project database so that the decision-makers are aware of the limitations.

Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used:

The Data Reviewer will review field notes and field Chain-of-Custody Records to determine that procedures specified in the FSP have been followed.

The CRA QA Officer or designated Data Reviewer will conduct a systematic review of the data for compliance with the established QC criteria based on the spike, duplicate, and blank results provided by the laboratory. Data validation will determine whether the procedures specified in the FSP and in this QAPP were implemented, the DQOs specified in this QAPP were attained, the specified Quantitation Limits were achieved, and the sample holding times were met. An evaluation of data accuracy, precision, sensitivity, and completeness, based on method-specific criteria, will be performed according to the following guidance documents:

- National Functional Guidelines for Organic Data Review (U.S. EPA, 1999).
- National Functional Guidelines for Inorganic Data Review (U.S. EPA 1994 and 2004)

Method specifications provided in the U.S. EPA-approved methods and laboratory SOPs will be used as a guide for validating data obtained for all analytes listed in this QAPP.

All forms will be checked. All raw data, including chromatograms, quantitation reports, data system printouts, and mass spectra for samples, standards, performance evaluation mixtures, blanks, and laboratory spikes/laboratory duplicates or MS/MSDs will be reviewed. A portion (~10 percent) of calculations such as spike recoveries, calibration response factors, analyte quantitation, etc., will be randomly spot-checked.

QAPP Worksheet #37
Usability Assessment

The procedures used to evaluate data include the following:

- All technical holding times will be checked for inorganic and organic analyses.
- Instrument performance check sample results, and initial and continuing calibration results, will be evaluated.
- Data for all blanks, surrogate spikes, matrix spikes/matrix spike duplicates, laboratory control samples, cleanup standards, internal and external standards, target compound identification and quantitation, and system performance checks will be reviewed.
- Sample calculations will be checked.
- Field precision will be determined from blind field duplicate data.
- Completeness of the data package will be checked to determine if all samples and analyses required by the QAPP were processed, that the procedures specified in the QAPP were implemented, and that all deliverables specified in the QAPP are included.
- The Data Reviewer will identify any out-of-control data points and data omissions, and will interact with the laboratory to correct data deficiencies.
- Decisions to repeat sample collection and analyses may be made by the CRA Project Manager based on the extent of the deficiencies and their importance in the overall context of the project.
- The CRA QA Officer will assess the usability of results against the DQOs.

QAPP Worksheet #37 (*continued*)
Usability Assessment

Describe the evaluative procedures used to assess overall measurement error associated with the project:

The data quality indicator (DQIs) used to evaluate conformance with the project DQOs are presented below.

DQIs are generally defined in terms of the following six parameters:

1. Representativeness
2. Comparability
3. Completeness
4. Precision
5. Accuracy
6. Sensitivity

Each parameter is defined below. Specific objectives for the site actions are presented in other sections of this QAPP, as referenced below.

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. Actions have been designed to assess the presence of chemical constituents at the time of sampling. The QAPP presents the rationale for sample quantities and location. This QAPP presents field sampling and laboratory analytical methodologies. Use of the prescribed field and laboratory analytical methods with associated holding times and preservation requirements is intended to provide representative data.

Comparability

Comparability is the degree of confidence with which one data set can be compared with another. Comparability between phases of the actions (if additional phases are required) will be maintained through consistent use of the sampling and analytical methodologies set forth in the QAPP, the established QA/QC procedures, and the use of appropriately trained personnel.

Completeness

Completeness is defined as a measure of the amount of valid data obtained from an event and/or investigation compared to the total amount that was obtained. This will be determined upon final assessment of the analytical results. Completeness of a field or laboratory data set will be calculated by comparing the number of valid sample results generated with the total number of results generated.

$$\text{Completeness} = \frac{\text{Number valid results}}{\text{Total number of results generated}} \times 100$$

As a general guideline, overall project completeness is expected to be at least 90 percent. The assessment of completeness will require professional judgment to determine data usability for intended purposes.

QAPP Worksheet #37 (*continued*)
Usability Assessment

Precision

Precision is a measure of the reproducibility of sample results. The goal is to maintain a level of analytical precision consistent with the objectives of the action. To maximize precision, sampling and analytical procedures will be followed. All work for the site actions will adhere to the established protocols presented in the QAPP. Checks for analytical precision will include the analysis of MS/MSDs, laboratory duplicates, and field duplicates. Checks for field measurement precision will include duplicate field measurements.

The precision of data will be measured by calculating the Relative Percent Difference (RPD) by the following equation:

$$RPD = \frac{(A-B)}{(A+B)/2} \times 100,$$

where

A = analytical result from one of two duplicate measurements,
B = analytical result from the second measurement.

Accuracy

Accuracy is a measure of how close a measured result is to the true value. Both field and analytical accuracy will be monitored through initial and continuing calibration of instruments. In addition, reference standards, MSs, blank spikes, and surrogate standards will be used to assess the accuracy of the analytical data.

Accuracy will be calculated in terms of percent recovery as follows:

$$\% \text{ Recovery} = \frac{A-X}{B} \times 100,$$

where

A = value measured in spiked sample or standard,

X = value measured in original sample,

B = true value of amount added to sample or true value of standard.

Sensitivity

Sensitivity is a quantitative measurement to determine if the analytical laboratory's procedures/methodologies and their associated MDLs can satisfy the project requirements as they relate to the project action limits. MDLs are updated annually by the laboratory.

QAPP Worksheet #37 (*continued*)
Usability Assessment

Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations), and anomalies:

The data validation report will address the following items:

- Overall quality and usability of the data
- Evaluation of QC data, including precision, accuracy, and completeness of the data
- Potential sample contamination due to blank contributions
- Assessment of laboratory and field records
- Actions regarding specific QC criteria exceedences

Laboratory-applied data qualifiers will be defined within the analytical data package received from the laboratory. The sample narrative will also detail quality control issues identified by the laboratory.

Data validation qualifiers that may be applied to the data include the following:

U The analyte/compound was analyzed for, but not detected. The associated value is the compound's Limit of Quantitation.

UJ The compound was not detected above the reported sample's Limit of Quantitation. However, the reported limit is approximate and may or may not represent the actual Limit of Quantitation.

J The compound was positively identified; however, the associated numerical value is an estimated concentration only.

R The sample results are rejected.

ATTACHMENTS

ATTACHMENT 1-5

NEW/REVISED LABORATORY STANDARD OPERATING PROCEDURES[1]:

W-15 (WATS SOP AM E-8270) SVOC Analysis (revised SOP to incorporate project defined RLs.)
W-25 (WATS SOP AM E-1312) SPLP Preparation method for Metals (new SOP).
W-26 (WATS SOP AM S-2340B) Hardness by Calculation (new SOP).
C-2 (CAS SMO-SCOC) Chain of Custody (revised SOP)
C-3 (CAS SOP SMO-GEN) Sample Receiving (revised SOP)
C-7 (CAS SOP MET-1630W) Methyl Mercury - in water (new SOP).
C-8 (CAS GEN-353.2) Nitrate/Nitrite (new SOP).
C-9 (CAS GEN-350.1) Ammonia (new SOP)
C-10 (CAS 365.3) Phosphorous (new SOP)
C-11 (CAS ADM-BAL.1) Balance (new SOP)
C-12 (CAS ADM-CA) Corrective Action (new SOP)

(1) The remainder of SOPs are included in the QAPP Revision 02, Addendum 03 that was submitted by RMT in November 2008.

1.0 SCOPE

1.1 This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from solid waste matrices, soils, sediments and ground water. It is based on the EPA's SWA-846 method 8270C and the Puget Sound Estuary Protocol (marine sediments). Direct injection of a sample may be used in limited applications. The method is normally used to determine the compounds in Table 1. Additional compounds that are less frequently determined are listed in Table 2.

1.2 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenyl amine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.3 The practical quantitation limit (PQL) of this method for determining an individual compound is approximately 330 µg/kg (wet weight) for soil/sediment samples, and 10 µg/L for ground water samples (see Table 5 for PQLs). PQLs will be higher depending upon dilution required and the moisture content of the sample.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

2.1 Water samples will be prepared utilizing continuous liquid/liquid extraction AC G-3520.

2.2 Soil samples will be prepared utilizing ultrasonic extraction AC G-3550.

2.3 Sediment samples will be prepared utilizing ultrasonic extraction AC G-3550 or soxhlet extraction AC G-3540. Sediment samples may require larger sample sizes and a modified calibration curve to achieve the required detection limits. Marine Sediment "PSEP" sample preparation method modifications are detailed in Appendix 3.

2.4 All soil and sediment samples will be cleaned up by gel permeation chromatography, AC G-3640-GPC.

2.5 Sediment samples may require a silica gel clean-up procedure, AC G-3630 if the analysis is for polyaromatic hydrocarbons only.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for chromatographic interferences caused by the preparative steps performed prior to analysis or instrumental procedures. Common sources of interferences include solvents, reagents and GPC carry-over from contaminated samples.

3.2 Contamination by GC carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 ESTIMATE OF ANALYTICAL TIME

4.1 Tuning and initial calibration require approximately 6 hours of instrument time prior to analysis of samples. If a valid calibration is available, approximately 2 hours is required for tuning and calibration verification.

4.2 Sample analysis requires approximately 1 hour of instrument time per sample. Data work up and reporting varies depending on sample type and reporting requirements. 1 to 2 hours should be anticipated per sample.

5.0 AMOUNT OF SAMPLE

5.1. Water samples require 1 liter of sample. An additional liter is required for each duplicate, matrix-spike or matrix-spike duplicate.

5.2 Soil samples require approximately 50 grams for sample extraction, pH determination and moisture determination. An additional 30 grams is required for each duplicate, matrix spike or matrix spike duplicate.

5.3 Sediment samples require the same amount of sample as soils unless low detection limits are required, such as for Puget Sound Protocol. Marine Sediment "PSEP" sample amount requirements are detailed in Appendix 3.

6.0 SAMPLE EXTRACT HANDLING AND STORAGE

6.1 Store sample extracts at 4°C until analysis.
6.2 Store sample extracts for 365 days following analysis at -10° to -20° C.

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6.3 Analyze sample extracts within 35 days.

7.0 APPARATUS AND MATERIALS

7.1 Gas chromatograph/mass spectrometer system – Hewlitt Packard 5972 MSD, capable of scanning from 35 to 500 amu every 1 sec., using 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 6 when 1µL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

7.2 Gas chromatograph - Hewlett Packard 5890 Series II with Hewlett Packard 5973A autosampler equipped with Split/Splitless injector.

7.3 Syringe - Hamilton 701ASN, 10µL.

7.4 Column - 30 m x 0.25 mm i.d., 0.25-µm film thickness silicone-coated, fused-silica capillary column (J&W Scientific DB-5MS is preferred but equivalent columns are acceptable).

7.5 Data system - Data analysis performed using Chemserver software on a HP/UX J5600 computer. Final data reports are generated in US-EPA CLP format (OLM 3.0) using Thruput Target and Envision software.

8.0 REAGENTS

8.1 All solvents used will be pesticide-residue grade or better.

8.2 Standard solutions - Standard solutions are purchased as certified solutions.

8.2.1. Commercially certified stock standards are used with the exception of alpha-terpineol. See standards preparation AC G-ORGSTD for standard preparation procedures. If the compound purity is assayed to be 96% or greater when stock solutions are prepared, the mass may be used without correction to calculate the concentration of the stock standard.

8.2.2. Secondary standard solutions will be stored at 4°C and protected from light. Stock standard solutions will be stored at -10° to -20°C and protected from light. All standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards or samples from them. The level of the solution in the container should be marked after each use so any evaporation can be detected.

8.2.3. The stock standard solutions must be replaced according to the manufactures expiration date. Working standards are replaced after 1 year or at the stocks expiration date (whichever is less), or sooner, if comparison with quality control check-samples indicates a problem.

8.2.4. Internal standard solutions - The internal standards used are listed in Table 3. The internal standard spiking solution will contain each standard at a concentration of

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2,000 ng/µL. Each sample extract undergoing analysis should be spiked with 1 µL of the internal standard solution per 100 µL of sample extract, resulting in a concentration of 20 ng/µL of each internal standard with a 1000-µL final extract volume.

8.2.5. GC/MS tuning standard consists of a methylene chloride solution containing 25 ng/µL of decafluorotriphenylphosphine (DFTPP).

8.2.6. Calibration standards

a. A minimum of five calibration standards should be prepared.

b. The normal concentrations of the calibration standards will be 10 µg/mL, 25 µg/mL, 40 µg/mL, 60 µg/mL and 80 µg/mL. If decreased detection limits are required, the additional calibration standards may be prepared down to a minimum concentration of 1 µg/mL.

c. Each standard contains each analyte for detection by this method (e.g., all of the compounds listed in Table 1 will be included). Compounds in Table 2 and selected additional compounds may be included if method performance criteria can be met.

d. Each aliquot of calibration standard is spiked with 1 µL of the internal standard solution per 100 µL of solution prior to analysis.

8.2.7. Surrogate standards - The six surrogate compounds used are listed in Table 3. 2-Chlorophenol-d4 and 1,2-Dichlorobenzene-d4 are also listed and may be used as alternate surrogate standards. The acid surrogates (phenolic) are spiked to achieve a final concentration of 75 µg/mL. The base/neutral surrogates are spiked to achieve a final concentration of 50 µg/mL. The extraction procedures provide instruction for preparing and adding surrogate spikes.

8.2.8. Laboratory control spike compounds (LCS) and matrix-spike compounds are listed in Table 11. Full-target compound laboratory control spikes (FLCS) and matrix spike compounds are listed in Table 1 (Due to the cost involved, FLCS are not analyzed unless requested by the client). Extraction procedures provide instruction for preparing and adding spike solutions.

9.0 PROCEDURE

See Section 2, Summary of Method, for appropriate extraction methods.

9.1 GC/MS operating conditions:

9.1.1. Mass range: 35-500 amu

9.1.2. Scan time: 0.9 sec/scan; 0.1 sec interscan time

9.1.3. Initial column temperature and hold time: 40° C for 1 minute

Note: If N-nitrosodimethylamine is to be determined, the initial temperature must be reduced to 35° C and the initial hold time must be extended to approximately 5 minutes.

9.1.4. Column temperature program: 40-320° C at 8° C/min

9.1.5. Final column temperature hold: 1-3 minutes @ 320° C

9.1.6. Injector temperature: 270° C

9.1.7. Transfer line temperature: 250° C

9.1.8. Source temperature: 180° C

9.1.9. Injector: Grob-type, splitless

9.1.10. Sample volume: 1 µL

9.1.11. Carrier gas: Helium at 30 cm/sec

9.2 Instrument Tune - GC/MS system must be hardware-tuned to meet the criteria in Table 5 for a 50-ng injection of DFTPP. Analyses may not begin for any standards or samples until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. It is suggested that the spectra for DFTPP be generated using a scan range ± 1 scan number from the scan number closest the total ion current maximum for DFTPP. Mass spectrometer conditions must be identical for subsequent analysis of standards, samples, QC samples and blanks associated with the DFTPP analysis.

9.3 Injector and Column maintenance

9.3.1. The injector sleeve should be clean and compound breakdown or adsorption should be minimized.

9.3.2. The capillary column should be in good condition, with minimal tailing noted for reactive compounds, such as pentachlorophenol.

9.4 The internal standards should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the internal standards specified in Table 3 to calculate compound concentrations.

9.5 Initial Calibration

9.5.1. Tune instrument as outlined in Section 9.2 above.

9.5.2. Analyze 1 µL of five or more calibration standards (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes.

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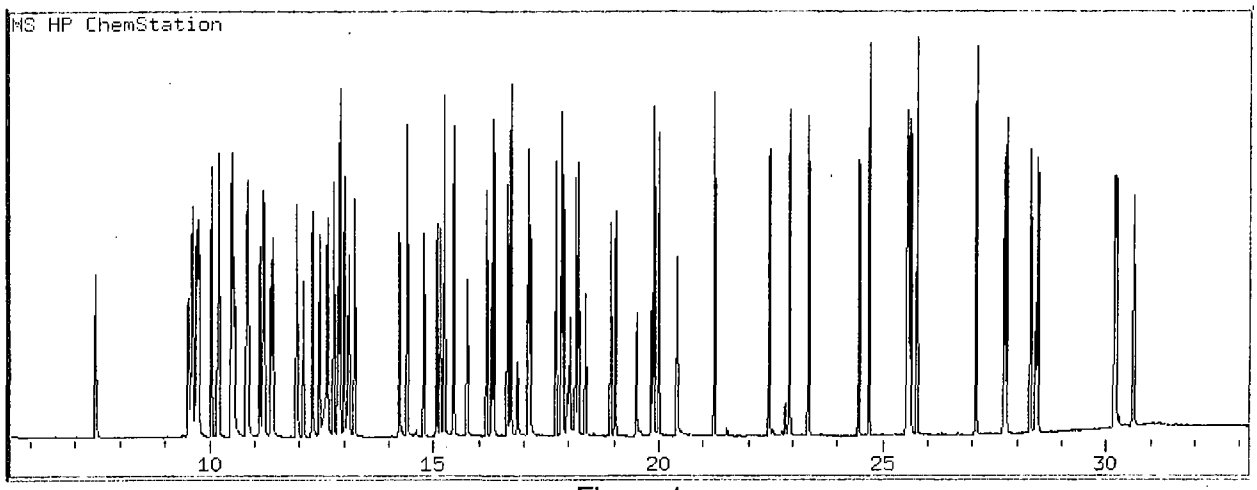

Figure 1

9.5.3. Calculate response factors (RFs) for each compound as shown below:

RF = (AxCis)/(AisCx)

where:

Ax = Area of the characteristic ion for the compound being measured.

Ais = Area of the characteristic ion for the specific internal standard.

Cx = Concentration of the compound being measured (µg/µL).

Cis = Concentration of the specific internal standard (µg/µL).

9.5.4.

a. Calculate the average RF and the percent relative standard deviation for each compound. If the RSD of any target compound is 15 % or less, the average relative response factor may be used for quantitation. If the RSD is greater than 15 %, Option 1 must be used:

Option 1 – Calculate a linear calibration using least-squares regression for each compound exceeding the 15 % RSD criteria. The correlation coefficient, r, must be greater than or equal to 0.99.

If the correlation coefficient, r, is less than 0.99, Option 2 must be used:

Option 2 – Calculate a non-linear calibration using a quadratic- or third-order polynominal regression for each compound exceding the 15 % RSD criteria. The coefficient of the determination, COD, must be greater than or equal to 0.99. **Note: SW-846 requires six calibration standards for second-order polynominals and seven calibration standards for third-order polynominals.**

If the coefficient of the determination, COD, is less than 0.99, Option 3 must be used:

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Option 3. - Calculate the mean of the RSD values for all analytes in the calibration. If it is less than or equal to 15%, the initial calibration is valid. Note: A summary report indicating compounds that exceeded the 15% RSD criteria and the results of the mean RSD calculation is required.

b. The %RSD for each individual Calibration Check Compound (CCC) (see Table 6) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. If the CCCs are not included in the project compound list, all compounds must meet the 30% RSD criteria.

9.5.5. A system-performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCS) are: N-nitroso-di-n-propylamine; hexachlorocyclo-pentadiene; 2, 4-dinitro-phenol; and 4-nitrophenol. The minimum acceptable average RF for these compounds is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

9.6 Daily GC/MS calibration

9.6.1. Prior to analysis of the daily calibration check, the GC/MS tuning standard must be analyzed and meet performance criteria as in 9.2.

9.6.2. A 50-µg/mL calibration standard containing each compound of interest, including all required surrogates, must be performed every 12 hours immediately following DFTPP during analysis. Compare the response factor data from the standards every 12 hours with the average response factor from the initial calibration for a specific instrument as per the SPCC, and CCC criteria in 9.6.3 and 9.6.4.

9.6.3. System Performance Check Compounds (SPCCs): A system performance check must be made during every 12-hour shift. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column and active sites in the column or chromatographic system. This check must be met before analysis begins.

9.6.4. Calibration Check Compounds (CCCs): After the system performance check is met, CCCs listed in Table 6 are used to check the validity of the initial calibration. For compounds using an average response factor calculate the percent difference using:

$$\%\,\text{Difference} = \frac{(RF_I - RF_C)}{\overline{RF_I}} \times 100$$

where:

$\overline{RF_I}$ = average response factor from initial calibration.

RF_c = response factor from current verification check standard.

For compounds using a linear or non-linear calibration curve, calculate the percent drift using:

$$\%\,\text{Drift} = \frac{(\textit{Calculated concentration - Theoretical concentration})}{\textit{Theoretical concentration}} \times 100$$

Where: the calculated concentration is determined using the mean calibration factor.

If the percent difference for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (> 20% difference for any one CCC), corrective action must be taken. If the CCCs are not included in the project compound list, all compounds must meet the 20% RSD criteria. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before sample analysis begins.

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

9.7 GC/MS analysis

9.7.1. The extract may be screened on a GC/FID or GC/PID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

9.7.2. Spike the sample extract or an aliquot of the sample extract with 1 µL of the internal standard solution (8.2.4) per 100 µL of sample extract, just prior to analysis.

9.7.3. Analyze the sample extract by GC/MS using the same conditions as were used for the initial and continuing calibration.

9.7.4. If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 20 ng/µL of each internal standard in the extracted volume. The diluted extract must be re-analyzed.

9.7.5. After analysis, store the extracts at 4° C, protected from light, in vials equipped with unpierced Teflon lined septa.

9.8 Data interpretation

9.8.1. Qualitative analysis

a. An analyte is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the GC/MS using the same operating conditions and DFTPP tune conditions as are used for sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component, and (2) correspondence of the sample component and the standard component mass spectrum.

b. The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hours as the sample. The RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

c. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum.

d. The relative intensities of ions specified should agree within ± 20% between the standard and sample spectra.

e. If these criteria are not met, but, in the opinion of the mass spectral specialist, the analyte is detected in the sample, the analyte will be reported.

f. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral specialist assign a tentative identification. Guidelines for making tentative identification are:

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

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

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

viii. 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.

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v. 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 peaks. Data system library reduction programs can sometimes create these discrepancies.

9.8.2. Quantitative analysis

a. When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standards to be used for each compound are listed in Table 7. If the compound does not appear in Table 7, the internal standard with a retention time nearest the retention time of that of a given analyte should be used.

b. Calculate the concentration of each identified analyte in the sample as follows:

Water

$$\text{Concentration}(\mu g/L) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RF})(V_o)(V_i)}$$

where:

A_x = Area of characteristic ion for the compound being measured.

I_s = Amount of internal standard injected (ng).

V_t = Volume of total extract, taking into account dilutions (i.e.; a 1 into 10 dilution of a 1-mL extract will mean Vt = 10,000 µL. If half the base/neutral extract and half the acid extract are combined, Vt = 2,000).

A_{is} = Area of characteristic ion for the internal standard.

$\overline{RF}$ = Average Response factor for compound being measured (See IX.F.4).

V_o = Volume of water extracted (mL).

V_i = Volume of extract injected (µL).

Sediment/Soil Sludge (dry-weight basis)

$$\text{Concentration}(\mu g/kg) = \frac{(A_x)(I_s)(V_t)}{(A_{is})(\overline{RF})(V_i)(W_s)(D)}$$

where:

A_x, I_s, V_t, A_{is}, $\overline{RF}$, V_i - Are the same as for water.

W_s = Mass of sample extracted or diluted, in grams.

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D = (100 - % moisture)/100, or 1 for a wet-weight (as-received) basis.

c. Where applicable, an estimate of concentration for non-calibrated components in the sample (tentatively identified compounds) should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

d. Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

e. Report results less than 10 parts-per-billion (PPB) to one significant figure. Report results greater than 10 PPB to two significant figures.

10.0 QUALITY CONTROL

10.1 Each day that an analysis is performed, DFTPP tune standard and the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are:

10.1.1. Does the air leak spectrum look ok? Is there evidence of an injector/septum leak?

10.1.2. Does FC43 calibration gas look normal? Are the ratios of m/z's 69, 131, 219 and 502 correct? Does the resolution look normal?

10.1.3. Does DFTPP meet criteria in Table 5 easily?

10.1.4. Do the chromatograhic peaks look normal for DFTPP and for the daily calibration standard?

10.1.5. Is the response obtained comparable to the response from previous DFTPP analyses and daily calibration analyses?

If any of the above do not appear normal, make appropriate corrections before attempting to analyze samples.

10.2 Required instrument QC before samples may be analyzed.

10.2.1. The GC/MS system must be tuned to meet the DFTPP specifications in Table 5.

10.2.2. Before processing any samples, the analyst should demonstrate, through the analysis of the method blank associated with the samples, that interferences from the analytical system and sample extraction are under control. Each set of samples that is extracted will be extracted with a method blank. The blanks must be carried through all stages of sample preparation and measurement with the samples.

10.2.3. There must be an initial calibration of the GC/MS system as specified in 9.5.

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10.2.4. The GC/MS system must meet the SPCC criteria specified in 9.6.3 and the CCC criteria in 9.6.4, each 12-hour period.

10.3 To establish the ability to generate acceptable accuracy and precision, the analyst must perform an initial demonstration of precision and accuracy (IPAR) as outlined in SOP, OQ-TRAIN.

10.3.1. A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 100 µg/mL in acetone. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

10.3.2. Using a gas tight syringe, prepare QC reference samples at a concentration of 100 µg/L by adding 1.00 mL of QC reference sample concentrate to each of four 1-L aliquots of water.

10.3.3. Analyze the well-mixed QC reference samples according to the method, beginning in section 9 with extraction of the samples.

10.3.4. Calculate the average recovery (x) in µg/L, and the standard deviation (s) of the recovery in µg/L, for each analyte of interest using the four results.

10.3.5. For each analyte, compare s and x with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 9. If s and x for all analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual x falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in Table 9 present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are analyzed.

10.3.6. When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for all analytes of interest beginning with 9.6. Repeated failure may require recalibration, beginning with 9.5.

10.4 The laboratory must analyze a reagent blank for each analytical batch (up to a maximum of 20 samples/batch, except for samples required under regulation which need QC every 10 samples), and should analyze a Laboratory Control Spike (LCS) for each analytical batch. A matrix spike and matrix spike duplicate should be analyzed for each 20 samples, except for samples required under regulation. Regulatory samples need QC every 10 samples. Matrix spikes may not be analyzed with each extraction batch.

Compare the percent recovery (p_s) for each analyte in the LCS with the laboratory generated QC charts (generated in 10.5.1a). If the recovery of any analytes of interest falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem identified and corrected. The analytical result for that analyte in the unspiked sample is suspect and, if possible, the samples associated with the LCS should be reanalyzed.

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10.5 As part of the QC program for the laboratory, method accuracy and precision for each matrix studied must be assessed and records must be maintained.

10.5.1. To determine acceptable accuracy and precision limits for LCS samples the following procedure should be performed.

a. After the analysis of five LCS (of the same matrix), calculate the average percent recovery (p) and the standard deviation of the percent recovery (s_p). Plot p, with a percent recovery interval of $p - 2 s_p$ to $p + 2 s_p$, with s the control limit and $p - 3 s_p$ to $p + 3 s_p$ as the action limit. (For example, if p = 90% and s_p = 10%, the control limit is 70-110% and the action limit is 60-120%.) Update the recovery charts for each analyte on a regular basis (e.g.; after each ten new measurements).

b. Only the twenty most recent LCS should be used to generate the QC limits.

c. For aqueous and soil matrices, these laboratory established LCS action limits may, if applicable, be compared with the control limits listed in Table 11.

10.5.2. To determine acceptable accuracy and precision limits for surrogate standards the following procedure will be performed.

a. After the analysis of five method blanks (of the same matrix), calculate the average percent recovery (p) and the standard deviation of the percent recovery (s_p). Plot p with a percent recovery interval of $p - 2 s_p$ to $p + 2 s_p$ as the control limit and $p - 3 s_p$ to $p + 3 s_p$ as the action limit. (For example, if p = 90% and s_p = 10%, the control limit is 70-110% and the action limit is 60-120%.) Update the recovery charts for each analyte on a regular basis (e.g.; after each twenty new measurements).

b. For aqueous matrices, these laboratory established action limits should, if applicable, be compared with the control limits listed in Table 10. The limits given are multi-laboratory performance based limits from EPA 8270, Rev 1, for soil and aqueous samples. Therefore, the single-laboratory limits established in the recovery chart must fall within those given in Table 10 for these matrices.

c. If recovery is not within limits, the following procedures are required. Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance. Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem. If possible, re-extract and re-analyze the sample if none of the above are a problem or note the recovery problem in the report narrative.

10.6 An MDL Study will be performed at least once per year as outlined in SOP, AQ G-MDL.

11.0 REFERENCES

11.1 U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Method 625,' October 26, 1984.

11.2 U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

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11.3 Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63, 1983.

11.4 Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

11.5 "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

11.6 "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).

11.7 Burke, J.A. 'Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects,' Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

11.8 Lucas, S.V.; Kornfeld, R.A. "GC-MS Suitability Testing of RCRA Appendix VIII and Michigan List Analytes "; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, February 20, 1987, Contract No. 68-03-3224.

11.9 Engel, T.M.; Kornfeld, R.A.; Warner, J.S.; Andrews, K.D. 'Screening of Semivolatile Organic Compounds for Extractability and Aqueous Stability by SW-846, Method 3510"; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, June 5, 1987, Contract 68-03-3224.

11.10 U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, OLM1.8.

11.12 U.S. EPA Method 8270, Revision 1, December 1987.

12.0 REVISION HISTORY

12.1 7/17/07 – Updated references to SOPs and made small corrections to directions regarding which section to which one should refer.

12.2 6/19/09 – Updated reporting limits.

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Table 1 -- List of characteristic ions of semi-volatile compounds

Compound	CAS#	Primary Ion	Secondary Ions
Acenaphthene	83-32-9	154	153, 152
Acenaphthylene	208-96-8	152	151, 153
Anthracene	120-12-7	178	176, 179
Benz(a)anthracene	56-55-3	228	229, 226
Benzo(b)fluoranthene	205-99-2	252	253, 125
Benzo(k)fluoranthene	207-08-9	252	253, 125
Benzo(g,h,i)perylene	191-24-2	276	138, 277
Benzo(a)pyrene	50-32-8	252	253, 125
Bis(2-chloroethoxy)methane	111-91-1	93	95, 123
Bi-s(2-chloroethyl)ether	111-44-4	93	63, 95
Bis(2-chloroisopropyl)ether	39638-32-9	45	77, 121
Bis(2-ethylhexyl)phthalate	117-81-7	149	167, 279
4-Bromophenyl phenyl ether	101-55-3	248	250, 141
Butyl benzyl phthalate	85-68-7	149	91, 206
4-Chloroaniline	106-47-8	127	129
4-Chloro-3-methylphenol	59-50-7	107	144, 142
2-Chloronaphthalene	91-58-7	162	127, 164
2-Chlorophenol	95-57-8	128	64, 130
4-Chlorophehyl phenyl ether	7005-72-3	204	206, 141
Chrysene	218-01-9	228	226, 229
Dibenz(a,h)anthracene	53-70-3	278	139, 279
Dibenzofuran	132-64-9	168	139
Di-n-butylphthalate	84-74-2	149	150, 104
1,2-Dichlorobenzene	95-50-1	146	148, 111
1,3-Dichlorobenzene	541-73-1	146	148, 111
1,4-Dichlorobenzene	106-46-7	146	148, 111
3,3-Dichlorobenzidine	91-94-1	252	254, 126
2,4-Dichlorophenol	120-83-2	162	164, 98
Diethyl phthalate	84-66-2	149	177, 150
2,4-Dimethylphenol	105-67-9	122	107, 121
Dimethyl phthalate	131-11-3	163	194, 164
4,6-Dinitro-2-methylphenol	534-52-1	198	51, 105
2,4-Dinitrophenol	51-28-5	184	63, 154
2,4-Dinitrotoluene	121-14-2	165	63, 89
2,6-Dinitrotoluene	606-20-2	165	63, 89
1,2-Diphenylhydrazine	122-66-7	77	105, 182
Di-n-octylphthalate	117-84-0	149	167, 43
Fluoranthene	206-44-0	202	101, 203
Fluorene	86-73-7	166	165, 167
Hexachlorobenzene	118-74-1	284	142, 149
Hexachlorobutadiene	87-68-3	225	223, 227
Hexachlorocyclopentadiene	77-47-4	237	235, 272
Hexachloroethane	67-72-1	117	201, 199
Indeno(1,2,3-cd)pyrene	193-39-5	276	138, 227
Isophorone	78-59-1	82	95, 138

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Compound	CAS#	Primary Ion	Secondary Ions
2-Methylnaphthalene	91-57-6	142	141
2-Methylphenol	95-48-7	108	107, 79
4-Methylphenol	106-44-5	108	107, 79
Naphthalene	91-20-3	128	129, 127
2-Nitroaniline	88-74-4	65	92, 138
3-Nitroaniline	99-09-2	138	108, 92
4-Nitroaniline	100-01-6	138	108, 92
Nitrobenzene	98-95-3	77	123, 65
2-Nitrophenol	88-75-5	139	109, 65
4-Nitrophenol	100-02-7	139	109, 65
N-Nitrosodiphenylamine	86-30-6	169	168, 167
N-Nitrosodi-n-propylamine	621-64-7	70	42, 101, 130
Pentachlorophenol	87-86-5	266	264, 268
Phenanthrene	85-01-8	178	179, 176
Phenol	108-95-2	94	65, 66
Pyrene	129-00-0	202	200, 203
1,2,4-Trichlorobenzene	120-82-1	180	182, 145
2,4,5-Trichlorophenol	95-95-4	196	198, 200
2,4,6-Trichlorophenol	88-06-2	196	198, 200

Table 2 -- List of characteristic ions of semi-volatile compounds

Compound	CAS#	Primary Ion	Secondary Ions
Benzidine	92-87-5	184	92, 185
Benzoic acid	65-85-0	122	105, 77
Benzyl alcohol	100-51-6	108	79, 77
N-Nitrosodimethylamine	62-75-9	42	74, 44
3-Methylphenol	108-39-4	108	107, 79
Pyridine	110-86-1		

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Table 3 - Internal Standards and Surrogates

Compound	Primary Ion	Secondary Ions
Internal Standards		
1,4-Dichlorobenzene-d4	152	115
Naphthalene-d8	136	68
Acenaphthene-d10	164	162, 160
Phenanthrene-d10	188	94, 80
Chrysene-d12	240	120, 236
Perylene-d12	264	260, 265
Surrogates		
Phenol-d5	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
Nitrobenzene-d5	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
2-Chlorophenol-d4(alternate)	132	68, 134
1,2-Dichlorobenzene-d4(alternate)	152	115, 150

Table 4 - PQLs FOR SEMIVOLATILE ORGANICS[b]
(EPA METHOD 8270, 1987 Rev. 1)

	Practical Quantitation Limits[b]	
Semivolatiles	Ground Water µg/L	Low Soil/ Sediment µg/kg
Acenapthene	10	330
Acenaphthylene	10	330
Anthracene	10	330
Benz(a)anthracene	10	330
Benzo(b)fluoranthene	10	330
Benzo(k)fluoranthene	10	330
Benzoic acid	10	330
Benzo(g,h,i)perylene	10	330
Benzo(a)pyrene	10	330
Benzyl alcohol	10	330
Bis(2-chloroethoxy) methane	10	330
Bis(2-chloroethyl) ether	10	330
Bis(2-chloroisopropyl) ether	10	330
Bis(2-ethylhexyl)phthalate	10	330
4-Bromophenyl phenyl ether	10	330
Butyl benzyl phthalate	10	330
4-Chloroaniline,	10	330
4-Chloro-3-methylphenol	10	330
2-Chloronaphthalene	10	330

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Semivolatiles	Ground Water µg/L	Low Soil/ Sediment µg/kg
2-Chlorophenol	10	330
4-Chlorophenyl phenyl ether	10	330
Chrysene	10	330
Dibenz(a,h)anthracene	10	330
Dibenzofuran	10	330
Di-n-butylphthalate	10	ND
1,2-Dichlorobenzene	10	330
1,3-Dichlorobenzene	10	330
1,4-Dichlorobenzene	10	330
3,3'-Dichlorobenzidine	10	330
2,4-Dichlorophenol	10	330
Diethylphthalate	10	330
2,4-Dimethylphenol	10	330
Dimethyl phthalate	10	330
4,6-Dinitro-2-methylphenol	10	330
2,4-Dinitrophenol	10	330
2,4-Dinitrotoluene	10	330
2,6-Dinitrotoluene	10	330
Di-n-octyl phthalate	10	330
Fluoranthene	10	330
Fluorene	10	330
Hexachlorobenzene	10	330
Hexachlorobutadiene	10	330
Hexachlorocyclopentadiene	10	330
Hexachloroethane	10	330
Indeno(1,2,3-cd)pyrene	10	330
Isophorone	10	330
2-Methylnaphthalene	10	330
2-Methylphenol	10	330
3-Methylphenol	10	ND
4-Methylphenol	10	330
Naphthalene	10	330
2-Nitroaniline	10	330
3-Nitroaniline	10	330
4-Nitroaniline	10	ND
Nitrobenzene	10	330
2-Nitrophenol	10	330
4-Nitrophenol	10	330
N-Nitrosodiphenylamine	10	330
N-Nitroso-di-n-propylamine	10	330
Pentachlorophenol	10	330
Phenanthrene	10	330
Phenol	10	330
Pyrene	10	330
Pyridine	ND	ND

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Semivolatiles	Ground Water µg/L	Low Soil/ Sediment µg/kg
1,2,4-Trichlorobenzene	10	330
2,4,5-Trichlorophenol	10	330
2,4,6-Trichlorophenol	10	330

PQLs listed for soil/sediment are based on wet mass. Normally data is reported on a dry-weight basis; therefore, PQLs will be higher based on the % moisture in each sample based on a 30-g sample and gel permeation chromatography cleanup.

b Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.
ND - Not determined.
NA - Not applicable.

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Table 5 - DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17-23% of mass 442

Table 6 - CALIBRATION CHECK COMPOUNDS (CCC)

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenyl.ami-ne	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

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Table 7 - SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d4	Naphthalene-d8	Acenaghthene-d10
Benzyl alcohol	Benzoic acid	Acenaphthene
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	Acenaphthylene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	2,4-Dimethylphenol	Dimethyl phthalate
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrophenol
Hexachloroethane	Isophorone	2,4-Dinitrotoluene
2-Methylphenol	Naphthalene	2,6-Dinitrotoluene
4-Methylphenol	Nitrobenzene	Fluorene
N-Nitrosodimethylamine	Nitrobenzene-d8 (surr.)	2-Fluorobiphenyl (surr.)
N-Nitroso-di-n-propylamine	2-Nitrophenol	Hexachlorocyclopentadiene
Phenol	1,2,4-Trichlorobenzene	2-Nitroaniline
Phenol-d6 (surr.)		3-Nitroaniline
		4-Nitroaniline
		4-Nitrophenol
		1,2,4,5-Tetrachlorobenzene
		2,4,6-Tribromophenol (surr.)
		2,4,6-Trichlorophenol
		2,4,5-Trichlorophenol

Phenanthrene-d10	Chrysene-d12	Perylene-d12
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl)phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butylbenzylphthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	3,3'-Dichlorobenzidine	Di-n-octylphthalate
Fluoranthene	Pyrene	Indeno(1,2,3-cd)pyrene
Hexachlorobenzene	Terphenyl-dl4 (surr.)	
N-Nitrosodiphenylamine		
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		

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Table 8 - QC ACCEPTANCE CRITERIAa
(EPA METHOD 8270C, 1996 Rev. 3)

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for x (µg/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Anthracene	100	32.0	43.4-118.0	27.133
Benz(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
Bis(2-chloroethyl)ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl)phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octylphthalate	100	31.4	18.6-131.8	4-146
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147

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Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for x (µg/L)	Range p, p_s (%)
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in µg/L.
x = Average recovery for four recovery measurements, in µg/L.
p, p_s = Percent recovery measured.
D = Detected; result must be greater than zero.

a criteria from 40 CFR Part 136 for Method 625. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

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Table 9 - ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION
(EPA METHOD 8270C, 1996 Rev. 3)

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Acenaphthene	0.96C+0.19	0.15x-0.12	0.21x-0.67
Acenaphthylene	0.89C+0.74	0.24x-1.06	0.26x-0.54
Anthracene	0.80C+0.68	0.21x-0.32	0.27x-0.64
Benz(a)anthracene	0.88C-0.60	0.15x+0.93	0.26x-0.21
Benzo(b)fluoranthene	0.93C-1.80	0.22x+0.43	0.29x+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19x+1.03	0.35x+0.40
Benzo(a)pyrene	0.90C-0.13	0.22x+0.48	0.32x+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29x+2.40	0.51x-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18x+0.94	0.53x+0.92
Bis(2-chloroethyl)ether	0.86C-1.54	0.35x-0.99	0.35x+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16x+1.34	0.26x+2.01
Bis(2-chloroisopropyl)ether	1.03C-2.31	0.24x+0.28	0.25x+1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26x+0.73	0.36x+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13x+0.66	0.16x+0.66
2-Chloronaphthalene	0.89C+0.01	0.07x+0.52	0.13x+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20x-0.94	0.30x-0.46
Chrysene	0.93C-1.00	0.28x+0.13	0.33x-0.09
Dibenzo(a,h)anthracene	0.88C+4.72	0.30x+8.51	0.59x+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13x+1.16	0.39x+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20x+0.47	0.24x+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25x+0.68	0.41x+0.ll
1,4-Dichlorobenzene	0.73C-1.47	0.24x+0.23	0.29x+0.36
3,3-Dichlorobenzidine	1.23C-12.65	0.28x+7.33	0.47x+3.45
Diethyl phthalate	0.43+1.00	0.28x+1.44	0.52x+0.22
Dimethyl phthalate	0.20C+1.03	0.54x+0.19	1.05x-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12x+1.06	0.21x+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14x+1.26	0.19x+0.35
Di-n-octylphthalate	0.76C-0.79	0.21x+1.19	0.37x+1.19
Fluoranthene	0.81C+1.10	0.22x-0.73	0.28x-0.60
Fluorene	0.90C-0.00	0.12x+0.26	0.13x+0.61
Hexachlorobenzene	0.74C+0.66	0.18x-0.10	0.43x-0.52
Hexachlorobutadiene	0.71C-1.01	0.19x+0.92	0.26x+0.49
Hexachloroethane	0.73C-0.83	0.17x+0.67	0.17x+0.80
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29x+1.46	0.50x-0.44
Isophorone	1.12C+1.41	0.27x+0.77	0.33x+0.26
Naphthalene	0.76C+1.58	0.21x-0.41	0.30x-0.68
Nitrobenzene	1.09C-3.05	0.19x+0.92	0.27x+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27x+0.68	0.44x+0.47
Phenanthrene	0.87C+0.06	0.12x+0.57	0.15x+0.25
Pyrene	0.84C-0.16	0.16x+0.06	0.15x+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15x+0.85	0.21x+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23x+0.75	0.29x+1.31

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Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
2-Chlorophenol	0.78C+0.29	0.18x+1.46	0.28x+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15x+1.25	0.21x+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16x+1.21	0.22x+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38x+2.36	0.42x+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10x+42.29	0.26x+23.10
2-Nitrophenol	0.07C-1.15	0.16x+1.94	6.27x+2.60
4-Nitrophenol	0.61C-1.22	0.38x+2.57	0.44x+3.24
Pentachlorophenol	0.93C+1.99	0.24x+3.03	0.30x+4.33
Phenol	0.43C+1.26	0.26x+0.73	0.35x+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16x+2.22	0.22x+1.81

X'= Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_r'= Expected single analyst standard deviation of measurements at an average concentration of x, in µg/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in µg/L.

C = True value for the concentration, in µg/L.

x = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

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Table 10
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES
(EPA CLP SOW OLM 3.0)

Surrogate Compound	Water	Low/Medium Soil/Sediment
Nitrobenzene-d	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-dl4	33-141	18-137
1,2-Dichlorobenzene(advisory)	16-110	20-130
Phenol-d6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122
2-Chlorophenol-d4(advisory)	33-110	20-130

Table 11
LCS SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES
(EPA CLP SOW OLM 3.0)

Compound	%Recovery Water	RPD Water	%Recovery Soil	RPD Soil
Phenol	12-110	42	26-90	35
2-Chlorophenol	27-123	40	25-102	50
1,4-Dichlorobenzene	36-97	28	28-104	27
N-Nitroso-di-n-propylamine	41-116	38	41-126	38
1,2,4,-Trichlorobenzene	39-98	28	38-107	23
4-Chloro-3-methylphenol	23-97	42	26-103	33
Acenaphthene	46-118	31	31-137	19
4-Nitrophenol	10-80	50	11-114	50
2,4-Dinitrotoluene	24-96	38	28-89	47
Pentachlorophenol	9-103	50	17-109	47
Pyrene	26-127	31	35-142	36

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Appendix 1 - Weyerhaeuser MDL Study

Matrix: (soil/water) Water
MDL Aliquot: 500 (ul)
Concentrated Extract Volume: 500 (ul)
Injection Volume: 1.0 (ul)
Units: PPB (ug/L)

Date Extracted: 1/9/2004
Date Analyzed: 1/13/2004
Extraction analyst Jim Sanderson
GC/MS analyst Jim Sanderson

Analyte	A	B	C	D	E	F	G
Phenol	4.69	4.86	4.13	4.62	4.45	4.65	4.73
Bis(2-chloroethyl)ether	4.85	4.35	3.82	4.58	4.37	4.41	4.78
2-Chlorophenol	4.46	4.30	3.95	4.40	4.22	4.52	4.45
1,3-Dichlorobenzene	2.74	2.30	2.36	2.76	2.90	2.89	3.29
1,4-Dichlorobenzene	2.88	2.48	2.43	2.75	3.10	2.88	3.18
1,2-Dichlorobenzene	3.13	2.66	2.79	2.97	3.24	3.06	3.58
2-Methylphenol	4.26	4.16	3.77	3.78	4.39	3.94	4.00
2,2'-oxybis(1-chloropropane)	3.68	3.57	3.17	3.51	3.53	3.61	3.77
N-Nitrosodinpropylamine	4.48	4.58	3.99	4.20	4.53	4.27	4.62
4-Methylphenol	4.11	4.28	3.90	3.83	4.46	4.03	3.98
Hexachloroethane	2.20	1.83	1.86	2.14	2.37	2.33	2.70
Nitrobenzene	4.91	4.32	3.85	4.78	4.73	4.63	4.68
Isophorone	4.95	4.75	4.52	4.52	4.80	4.70	4.90
2-Nitrophenol	4.30	4.00	3.72	4.16	4.15	4.21	4.12
2,4-Dimethyphenol	2.28	2.39	2.04	1.53	3.31	1.71	1.60
Bis(2-chloroethoxy)methane	4.29	3.88	3.82	3.97	4.16	4.12	4.27
2,4-Dichlorophenol	4.49	4.50	3.96	4.50	4.56	4.36	4.43
1,2,4-Trichlorobenzene	2.92	2.53	2.63	2.95	3.26	3.03	3.32
Naphthalene	3.98	3.60	3.40	3.95	3.92	3.86	4.09
4-Chloroaniline	5.07	4.35	4.32	4.31	3.52	4.71	4.62
Hexachlorobutadiene	2.03	1.61	1.85	2.09	2.32	2.20	2.79
4-Chloro-3-Methylphenol	4.24	4.15	4.03	4.28	4.62	4.40	4.37
2-Methylnaphthalene	3.84	3.40	3.44	3.75	3.96	3.72	4.16
Hexachlorocyclopentadiene	<1	<1	<1	<1	<1	<1	<1
2,4,6-Trichlorophenol	4.51	4.35	4.17	4.38	4.22	4.20	4.31
2,4,5-Trichlorphenol	4.35	4.06	3.86	3.98	4.41	4.18	4.27
2-Chloronaphthalene	3.97	3.69	3.50	3.93	4.03	3.78	4.20
2-Nitroaniline	5.24	3.91	4.87	4.80	4.21	5.00	4.93
Acenaphthylene	4.24	4.08	3.90	4.33	4.31	4.31	4.36
2,6-Dinitrotoluene	4.88	4.20	4.49	4.52	4.64	4.75	4.66
3-Nitroaniline	4.48	4.39	4.54	4.63	4.59	4.76	4.66
Acenaphthene	4.23	3.92	3.74	4.12	4.23	4.16	4.23
2,4-Dinitrophenol	5.87	5.79	6.37	6.29	6.46	6.56	5.94
Dibenzofuran	4.49	3.96	4.18	4.50	4.47	4.47	4.45
4-Nitrophenol	5.42	4.86	5.56	5.67	5.94	5.68	5.34
2,4-Dinitrotoluene	5.16	4.51	5.28	5.11	5.13	5.13	5.27
Fluorene	4.51	3.85	4.16	4.41	4.58	4.58	4.52
Dimethylphthalate	4.98	4.46	4.61	4.60	4.61	4.64	4.71
Diethylphthalate	4.79	4.36	4.75	4.63	4.70	4.72	4.74
4-Chlorophenyl-phenylether	4.40	3.63	4.05	4.38	4.39	4.41	4.37

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser.

Matrix: (soil/water) Water
MDL Aliquot: 500 (ul)
Concentrated Extract Volume: 500 (ul)
Injection Volume: 1.0 (ul)
Units: PPB (ug/L)

Date Extracted: 1/9/2004
Date Analyzed: 1/13/2004
Extraction analyst Jim Sanderson
GC/MS analyst Jim Sanderson

Analyte	A	B	C	D	E	F	G
4-Nitroaniline	4.96	3.71	4.96	5.13	4.81	5.30	5.14
4,6-Dinitro-2-methylphenol	5.36	5.54	5.78	5.71	5.72	5.89	5.40
N-Nitrosodiphenylamine	4.93	4.70	4.59	4.54	3.49	4.75	5.04
4-Bromophenyl-phenylether	5.09	5.05	4.70	4.86	4.69	5.14	5.01
Hexachlorobenzene	5.13	5.03	4.51	4.70	5.07	4.88	4.98
Pentachlorophenol	5.64	6.04	5.94	6.23	6.50	6.44	6.07
Phenanthrene	5.29	4.94	4.93	5.10	5.24	5.15	5.24
Anthracene	5.01	4.75	4.84	4.98	4.87	5.24	5.01
Di-n-Butylphthalate	5.53	5.36	5.65	5.42	5.61	5.59	5.59
Fluoranthene	4.65	4.22	4.87	4.90	4.93	4.93	4.66
Pyrene	6.02	6.47	5.84	5.58	5.30	5.98	5.90
Butylbenzylphthalate	5.37	5.52	5.35	5.13	4.86	5.31	5.29
Benzo(a)Anthracene	5.38	5.34	5.40	5.30	5.14	5.45	5.47
3,3'-Dichlorobenzidine	3.30	2.87	3.04	2.86	0.51	2.72	3.03
Chrysene	5.56	5.57	5.56	5.50	5.34	5.52	5.80
bis(2-ethylhexyl)Phthalate	5.60	5.53	5.70	5.03	5.07	5.23	5.56
Di-n-octylphthalate	4.88	5.05	5.02	4.76	4.71	4.90	4.81
Benzo(b)fluoranthene	4.79	4.74	4.95	4.54	4.46	4.66	4.66
Benzo(k)fluoranthene	4.85	4.81	4.80	4.89	5.06	4.98	5.38
Benzo(a)pyrene	4.57	4.39	4.45	4.35	4.27	4.52	4.55
Indeno(1,2,3-cd)pyrene	4.54	4.45	4.49	4.48	4.60	4.51	4.47
Dibenzo(a,h)anthracene	4.43	4.43	4.40	4.26	4.41	4.38	4.39
Benzo(g,h,i)perylene	4.81	4.71	4.74	4.62	4.78	4.66	4.78
Carbazole	6.01	5.12	5.70	6.08	5.49	6.17	5.79
Aniline	4.89	4.96	4.70	4.12	1.48	4.95	4.65
Benzyl Alcohol	5.37	5.28	4.81	4.94	5.20	5.12	5.40
Benzoic Acid	4.77	5.11	4.93	5.12	6.07	5.22	4.87
Benzidine	<10	<10	<10	<10	<10	<10	<10
1,2-Diphenylhydrazine	4.99	5.10	4.61	4.82	4.62	4.86	5.06

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Matrix: (soil/water) Water
MDL Aliquot: 500 (ul)

Concentrated Extract Volume: 500 (ul)
Injection Volume: 1.0 (ul)
Units: PPB (ug/L)

Date Extracted: 1/9/2004
Date Analyzed: 1/13/2004
Extraction analyst Jim Sanderson
GC/MS analyst Jim Sanderson

Analyte	MEAN	STDEV	MDL	SPIKE	% Rec
Phenol	4.59	0.237	0.7	5	92
Bis(2-chloroethyl)ether	4.45	0.342	1.1	5	89
2-Chlorophenol	4.33	0.196	0.6	5	87
1,3-Dichlorobenzene	2.75	0.339	1.1	5	55
1,4-Dichlorobenzene	2.81	0.285	0.9	5	56
1,2-Dichlorobenzene	3.06	0.302	1.0	5	61
2-Methylphenol	4.04	0.237	0.7	5	81
2,2'-oxybis(1-chloropropane)	3.55	0.190	0.6	5	71
N-Nitrosodinpropylamine	4.38	0.233	0.7	5	88
4-Methylphenol	4.08	0.221	0.7	5	82
Hexachloroethane	2.20	0.303	1.0	5	44
Nitrobenzene	4.56	0.361	1.1	5	91
Isophorone	4.73	0.169	0.5	5	95
2-Nitrophenol	4.09	0.188	0.6	5	82
2,4-Dimethyphenol	2.12	0.620	1.9	5	42
Bis(2-chloroethoxy)methane	4.07	0.186	0.6	5	81
2,4-Dichlorophenol	4.40	0.204	0.6	5	88
1,2,4-Trichlorobenzene	2.95	0.294	0.9	5	59
Naphthalene	3.83	0.242	0.8	5	77
4-Chloroaniline	4.41	0.480	1.5	5	88
Hexachlorobutadiene	2.13	0.373	1.2	5	43
4-Chloro-3-Methylphenol	4.30	0.190	0.6	5	86
2-Methylnaphthalene	3.75	0.271	0.9	5	75
Hexachlorocyclopentadiene	<1	N.M.	N.M.	5	N.M.
2,4,6-Trichlorophenol	4.31	0.120	0.4	5	86
2,4,5-Trichlorphenol	4.16	0.201	0.6	5	83
2-Chloronaphthalene	3.87	0.233	0.7	5	77
2-Nitroaniline	4.71	0.472	1.5	5	94
Acenaphthylene	4.22	0.168	0.5	5	84
2,6-Dinitrotoluene	4.59	0.218	0.7	5	92
3-Nitroaniline	4.58	0.122	0.4	5	92
Acenaphthene	4.09	0.190	0.6	5	82
2,4-Dinitrophenol	6.18	0.310	1.0	5	124
Dibenzofuran	4.36	0.209	0.7	5	87
4-Nitrophenol	5.50	0.342	1.1	5	110
2,4-Dinitrotoluene	5.08	0.262	0.8	5	102
Fluorene	4.37	0.273	0.9	5	87
Dimethylphthalate	4.66	0.160	0.5	5	93
Diethylphthalate	4.67	0.145	0.5	5	93
4-Chlorophenyl-phenylether	4.23	0.295	0.9	5	85

Proprietary — Disclosure limited to persons confidentially bound to Weyerhaeuser.

Matrix: (soil/water) Water
MDL Aliquot: 500 (ul)

Concentrated Extract Volume: 500 (ul)

Injection Volume: 1.0 (ul)
Units: PPB (ug/L)

Date Extracted: 1/9/2004
Date Analyzed: 1/13/2004
Extraction analyst Jim Sanderson
GC/MS analyst Jim Sanderson

Analyte	MEAN	Std Dev	MDL	Amount Spiked	% Recovery
4-Nitroaniline	4.86	0.531	1.7	5	97
4,6-Dinitro-2-methylphenol	5.63	0.199	0.6	5	113
N-Nitrosodiphenylamine	4.58	0.511	1.6	5	92
4-Bromophenyl-phenylether	4.93	0.185	0.6	5	99
Hexachlorobenzene	4.90	0.223	0.7	5	98
Pentachlorophenol	6.12	0.297	0.9	5	122
Phenanthrene	5.13	0.146	0.5	5	103
Anthracene	4.96	0.158	0.5	5	99
Di-n-Butylphthalate	5.54	0.107	0.3	5	111
Fluoranthene	4.74	0.258	0.8	5	95
Pyrene	5.87	0.366	1.2	5	117
Butylbenzylphthalate	5.26	0.211	0.7	5	105
Benzo(a)Anthracene	5.35	0.111	0.3	5	107
3,3'-Dichlorobenzidine	2.62	0.948	3.0	5	52
Chrysene	5.55	0.136	0.4	5	111
bis(2-ethylhexyl)Phthalate	5.39	0.273	0.9	5	108
Di-n-octylphthalate	4.88	0.127	0.4	5	98
Benzo(b)fluoranthene	4.69	0.162	0.5	5	94
Benzo(k)fluoranthene	4.97	0.205	0.6	5	99
Benzo(a)pyrene	4.44	0.112	0.4	5	89
Indeno(1,2,3-cd)pyrene	4.51	0.051	0.2	5	90
Dibenzo(a,h)anthracene	4.39	0.059	0.2	5	88
Benzo(g,h,i)perylene	4.73	0.069	0	5	95
Carbazole	5.77	0.370	1.2	5	115
Aniline	4.25	1.26	3.9	5	85
Benzyl Alcohol	5.16	0.220	0.7	5	103
Benzoic Acid	5.16	0.433	1.4	5	103
Benzidine	<10	N.M.	N.M.	5	N.M.
1,2-Diphenylhydrazine	4.87	0.198	0.6	5	97

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Appendix 2 - TYPICAL SURROGATE AND LCS PERCENT RECOVERIES

PRECISION & ACCURACY
STUDY 8270

Date: 03/07/94
Data: 2SV40304A-2SV40304E
Method: 8270
Analyst: J. Leong
Extractionist: T. Sutherland
Extractionist: M. Luthy
Extraction Date: 2/22/94
Spiked: 50µg/L

Replicate #	% recovery (P) #1	#2	#3	#4	average (X) (% rec.)	Std.Dev. (s)	compliance	limit for s	Range for X (% rec.)	Range for P
PHENOL	53.7	55.5	53.9	58.3	55.4	2.1	Y	22.6	16.6-100.0	5-112
BIS(2-CHLOROETHYL)ETHER	73.9	78.1	78.9	69.2	75.0	4.4	Y	55	42.9-126.0	12-158
2-CHLOROPHENOL	62.4	65.2	61.1	65.1	63.4	2.0	Y	28.7	36.2-120.4	23-134
1,3-DICHLOROBENZENE	60.0	72.6	72.2	62.4	66.8	6.5	Y	41.7	16.7-153.9	d-172
1,4-DICHLOROBENZENE	61.8	72.0	72.0	62.9	67.1	5.6	Y	32.1	37.3-105.7	20-124
1,2-DICHLOROBENZENE	62.5	70.4	69.4	62.3	66.1	4.3	Y	30.9	48.6-112.0	32-129
2-METHYLPHENOL	73.8	77.5	74.2	74.4	75.0	1.7		NA		
2,2'-OXYBIS(1-CHLOROPROPANE)	83.1	86.7	84.8	74.7	82.3	5.3	Y	46.3	62.8-138.6	36-166
4-METHYLPHENOL	75.8	74.7	76.2	77.1	76.0	1.0		NA		
N-NITROSO-DI-N-PROPYLAMINE	79.4	81.5	81.9	73.2	79.0	4.0	Y	55.4	13.6-197.9	d-230

HEXACHLOROETHANE	57.3	75.6	75.4	65.6	68.5	8.8	Y	24.5	55.2-100.0	40-113
NITROBENZENE	73.6	78.0	75.8	67.2	73.6	4.7	Y	39.3	54.3-157.6	35-180
ISOPHORONE	79.7	82.3	83.4	73.5	79.7	4.4	Y	63.3	46.6-180.2	21-196
2-NITROPHENOL	78.4	82.7	78.4	84.7	81.0	3.1	Y	35.2	45.0-166.7	29-182
2,4-DIMETHYLPHENOL	59.9	52.4	63.8	50.1	56.5	6.4	Y	26.1	41.8-109.0	32-119
BIS(2-CHLOROETHOXY)METHANE	82.3	84.5	85.0	75.8	81.9	4.2	Y	34.5	49.2-164.7	33-184
2,4-DICHLOROPHENOL	72.3	76.5	72.0	77.6	74.6	2.9	Y	26.4	52.5-121.7	39-135
1,2,4-TRICHLOROBENZENE	70.0	81.0	80.5	71.0	75.6	5.9	Y	28.1	57.3-129.2	44-142
NAPHTHALENE	73.8	79.2	79.9	69.6	75.6	4.9	Y	30.1	35.6-119.6	21-133
4-CHLOROANILINE	78.3	81.3	83.7	72.9	79.0	4.7		NA		
HEXACHLOROBUTADIENE	66.0	82.6	81.9	71.3	75.4	8.2	Y	26.3	37.8-102.2	24-116
4-CHLORO-3-METHYLPHENOL	76.5	78.7	77.9	77.2	77.5	0.9	Y	37.2	40.8-127.9	22-147
2-METHYLNAPHTHALENE	77.6	80.3	81.9	74.7	78.6	3.2		NA		
HEXACHLOROCYCLOPENTADIENE	3.0	2.4	4.1	3.9	3.4	0.8		NA		
2,4,6-TRICHLOROPHENOL	77.8	81.4	73.9	83.3	79.1	4.1	Y	31.7	52.4-129.2	37-144
2,4,5-TRICHLOROPHENOL	76.7	76.0	70.8	74.9	74.6	2.7		NA		
2-CHLORONAPHTHALENE	80.2	84.1	84.9	77.4	81.6	3.5	Y	13.0	64.5-113.5	60-118
2-NITROANILINE	78.4	81.3	83.5	74.2	79.3	4.0		NA		
DIMETHYLPHTHALATE	36.4	68.3	71.9	67.5	61.0	16.5	Y	23.2	d-100.0	d-112
ACENAPHTHYLENE	76.4	79.3	81.0	73.7	77.6	3.2	Y	40.2	53.5-126.0	33-145

2,6-DINITROTOLUENE	80.9	85.9	90.2	80.7	84.4	4.6	Y	29.6	68.1-136.7	50-158
3-NITROANILINE	88.9	92.9	95.6	88.4	91.5	3.4		NA		
ACENAPHTHENE	77.4	80.3	80.3	73.0	77.8	3.4	Y	27.6	60.1-132.3	47-145
2,4-DINITROPHENOL	81.1	86.3	79.6	92.0	84.7	5.6	Y	49.8	d-172.9	d-191
4-NITROPHENOL	73.8	78.2	67.0	74.9	73.5	4.7	Y	47.2	13.0-106.5	d-132
DIBENZOFURAN	79.5	83.0	85.0	76.6	81.0	3.7		NA		
2,4-DINITROTOLUENE	82.1	83.8	87.7	80.7	83.6	3.0	Y	21.8	47.5-126.9	39-139
DIETHYLPHTHALATE	74.5	87.6	92.2	86.0	85.1	7.5	Y	26.5	d-100.0	d-114
4-CHLOROPHENYLPHENYLETHER	88.9	93.1	95.6	87.7	91.3	3.7	Y	33.4	38.4-144.7	25-158
FLUORENE	80.8	81.8	85.8	78.6	81.7	3.0	Y	20.7	71.6-108.4	59-121
4-NITROANILINE	86.6	96.3	98.2	92.5	93.4	5.1		NA		
4,6-DINITRO-2-METHYLPHENOL	73.9	76.9	72.1	78.3	75.3	2.8	Y	93.2	53.0-100.0	d-181
N-NITROSODIPHENYLAMINE	78.5	96.4	98.6	90.5	91.0	9.0		NA		
4-BROMOPHENYLPHENYLETHER	94.6	98.3	101.3	91.8	96.5	4.2	Y	23	64.9-114.4	53-127
HEXACHLOROBENZENE	90.2	94.9	98.3	88.7	93.0	4.4	Y	24.9	7.8-141.5	d-152
PENTACHLOROPHENOL	86.9	92.0	82.1	92.7	88.5	4.9	Y	48.9	38.1-151.8	14-176
PHENANTHRENE	82.1	83.9	86.2	77.7	82.5	3.6	Y	20.6	65.2-108.7	54-120
ANTHRACENE	84.5	86.5	90.0	80.4	85.4	4.0	Y	32	43.4-118.0	27-133
CARBAZOLE	118.8	127.5	133.2	123.5	125.8	6.1		NA		
DI-N-BUTYLPHTHALATE	87.2	92.0	96.7	86.1	90.5	4.9	Y	16.7	8.4-111.0	1-118
FLUORANTHENE	82.0	85.2	88.1	79.5	83.7	3.8	Y	32.8	42.9-121.3	26-137
PYRENE	86.1	91.1	87.1	82.1	86.6	3.7	Y	25.2	69.6-100.0	52-115

BUTYLBENZYLYPHTHALATE	88.0	95.8	91.6	84.7	90.0	4.7	Y	23.4	d-139-9	d-152
3,3'-DICHLOROBENZIDENE	129.4	150.0	146.8	132.3	139.6	10.3	Y	71.4	8.2-212.5	d-262
BENZO(A)ANTHRACENE	83.2	93.6	84.3	82.2	85.8	5.3	Y	27.6	41.8-133.0	33-143
CHRYSENE	83.1	88.7	88.2	80.9	85.2	3.8	Y	48.3	44.1-139.9	17-168
BIS(2-ETHYLHEXYL)PHTHLATE	88.0	94.7	90.3	83.0	89.0	4.9	Y	41.1	28.9-136.8	8-158
DIOCTYLPHTHALATE	81.9	83.8	89.6	79.0	83.5	4.5	Y	31.4	18.6-131.8	4-146
BENZO(B)FLUORANTHENE	79.9	83.7	85.6	77.1	81.6	3.8	Y	38.8	42.0-140.4	24-159
BENZO(K)FLUORANTHENE	73.8	70.3	79.0	72.0	73.8	3.7	Y	32.3	25.2-145.7	11-162
BENZO(A)PYRENE	79.7	81.4	85.2	78.6	81.2	2.9	Y	39	31.7-148.0	17-163
INDENO(1,2,3-CD)PYRENE	84.3	92.0	88.8	82.4	86.9	4.4	Y	44.6	d-150.9	d-171
DIBENZ(A,H)ANTHRACENE	86.0	93.5	94.7	86.7	90.2	4.5	Y	70	d-199.7	d-227
BENZO(G,H,I)PERYLENE	80.6	83.5	88.2	80.1	83.1	3.7	Y	58.9	d-195.0	d-219

Appendix 3 - METHOD MODIFICATIONS FOR MARINE SEDIMENT "PSEP."

INTRODUCTION – Analytical Method AM E-8270 requires modifications to address specific low reporting limits and reporting units.

MODIFICATIONS – The following modifications are required:

I. EXTRACTION PROCEDURE RECOMMENDATION
II. ORGANIC CARBON
III. REPORTING LIMITS
IV. SAMPLE AMOUNT
V. EXTRACTION MODIFICATIONS
VI. CALIBRATION STANDARDS
VII. REPORTING UNITS

I. EXTRACTION PROCEDURE RECOMMENDATION

The recommended extraction method for marine sediments is soxhlet extraction, SOP AC G-3540. Ultrasonic extraction, SOP AC G-3350, is an acceptable alternative; however comparable recoveries to SOP AC G-3540 must be confirmed.

II. ORGANIC CARBON

A. Numerical reporting values for organic analytes will be normalized based on organic carbon.

B. The analysis for total organic carbon, as well as the percent moisture will be performed by Group 4 (Conventional Group).

C. Total organic carbon and percent moisture data will be used to calculate sample size.

III. REPORTING LIMITS

The reporting limits for marine sediment is analyte specific. The reporting limits are detailed in Table A1. However, a 380-µg/kg organic carbon reporting limit will be used as the basis for determining sample size, final sample extract volume, and calibration standard concentration.

IV. SAMPLE AMOUNT

Use the following formula to determine sample size:

$$\text{Sample size (g)} = \frac{(LS)(F_v)(2)}{(380)(D)(TOC)}$$

Where:

LS = Concentration of the lowest calibration standard in ug/mL. For marine sediment the low calibration standard concentration is 1.0 ug/mL.

F_V = Final volume of the sample extract. For marine sediment the final extract volume is 250 microliters.

The value of 2 is used due to GPC loop loss.

The value of 380 is the resultant analyte concentration in PPB, OC normalized (specified reporting limit).

D = (100 - % moisture in sample)/100.

TOC = percent total organic carbon in the dry weight sample (1 percent TOC = 0.01).

V. EXTRACTION MODIFICATIONS

If the calculated sample size is greater than 60 g the following extraction modifications will need to be made:

A. Weigh the sample into two equal portions. Spike each portion with one half of the surrogate solution, and/or spiking solution. For example, suppose the total sample size is 150 g and one mL of spiking solution is required. The procedure modification would require two sample portions weighing 75 g each. 500 µL of the spiking solution would be added to each sample portion.

B. Combine the sample fraction extracts prior to sample concentration.

C. After GPC cleanup, concentrate the sample extract to 200 µL. Transfer the sample extract to an amber GC vial containing a 300-µL GC vial insert (or equivalent insert). Rinse the concentration tube with small amounts of methylene chloride and combine with the extract in the insert. Continue until a final extract volume of 250 µL is achieved.

VI. CALIBRATION STANDARDS

Include an initial calibration standard at a concentration of 1.0 µg/mL. Verify the curves are valid for the following analytes: 1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, hexachlorobenzene.

VII. REPORTING UNITS

Report the analyte concentration in mg/kg TOC. Include the concentration for LPAH, HPAH compounds and total benzofluoranthenes. The LPAH criterion represents the sum of the following "low molecular polynuclear aromatic hydrocarbon" compounds: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene. The HPAH criterion represents the sum of the following "high molecular polynuclear aromatic hydrocarbon" compounds: fluoranthene, pyrene, benz(a)anthracene, chrysene, total benzofluoranthenes, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene. The total benzofluoranthenes criterion represents the sum of the concentrations of "B," "J," and "K" isomers.

Table A1. Reporting limits for marine sediment.

Chemical Parameter	mg/kg Organic Carbon
LPAH	370
Naphthalene	99
Acenaphthylene	66
Acenaphthene	16
Fluorene	23
Phenanthrene	100
Anthracene	220

Chemical Parameter	mg/kg Organic Carbon
Bis(2-ethylhexyl) Phthalate	47
Di-n-octyl Phthalate	58
Dibenzofuran	15
Hexachlorobutadiene	3.9
N-Nitrosodiphenylamine	11

Chemical Parameter	mg/kg Organic Carbon
2-Methylnaphthalene	38
HPAH	960
Fluoranthene	160
Pyrene	1000
Benz(a)anthracene	110
Chrysene	110
Total Benzofluoranthene	230
Benzo(a)pyrene	99
Indeno(1,2,3-cd)pyrene	34
Dibenz(a,h)anthracene	12
Benzo(g,h,i)perylene	31
1,2-Dichlorobenzene	2.3
1,4-Dichlorobenzene	3.1
1,2,4-Trichlorobenzene	0.81
Hexachlorobenzene	0.38
Dimethyl Phthalate	53
Diethyl Phthalate	61
Di-n-butyl Phthalate	220
Butyl Benzyl Phthalate	4.9

Chemical Parameter	mg/kg Organic Carbon
Chemical Parameter	**µg/kg Dry Weight(PPB)**
Phenol	420
2-Methylphenol	63
4-Methylphenol	670
2,4-Dimethyl Phenol	29
Pentachlorophenol	360
Benzyl Alcohol	57
Benzoic Acid	650

Synthetic Precipitation Leaching Procedure (SPLP)

Process Owner (TS/PM/OM/LM)	Not valid without colored "Controlled" stamp (unless printing date appears)
Dan Deprez	Valid one calendar day from , expires at midnight. (Also valid for the process' duration.)
Assignment	Reviewed June 1, 2009 by Christine Devine
Electronic only unless colored "Controlled" stamp is present	

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1.0 SCOPE

1.1 The SPLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual analytes are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, the SPLP extraction itself need not be run.

1.3 If an analysis of any one of the liquid fractions of the SPLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be equal to or above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte equals or exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.0 SUMMARY OF METHOD

2.1 For liquid wastes (i.e., those containing less than 0.5 % dry solid material), the waste, after filtration through a 0.6 - 0.8 um glass fiber filter, is defined as the SPLP extract.

2.2 For wastes containing greater than or equal to 0.5 % solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the mass of the solid phase. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater, the extraction fluid employed is a pH 4.2 solution. A special extractor vessel is used when testing for volatile analytes. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 - 0.8 um glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 INTERFERENCES

Potential interferences that may be encountered during analysis are discussed in the individual analytical methods. The pH of the extraction fluid has the greatest impact on the metals results and therefore the extraction fluid must have the pH within ± 0.05 of the specified pH. Poor precision is due to sample homogeneity.

4.0 ESTIMATE OF ANALYTICAL TIME

This method has an 18 hour extraction and therefore can take up to 24 hours.

5.0 AMOUNT OF SAMPLE REQUIRED

The SPLP places requirements on the minimal size of the sample, depending upon the physical state of the waste and the analytes of concern. A 5-gram aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile analyte extraction procedure. Another 100- to 10,000-g aliquot may be needed to actually conduct the nonvolatile extraction. If volatile organics are of concern, another 25- to 500-g aliquot may be needed. Quality control measures may require additional aliquots. Further, extra sample should be collected just in case something goes wrong with the initial attempt to conduct the test.

6.0 SAMPLING, SAMPLE HANDLING, AND PRESERVATION

6.1 Vinyl gloves will be worn when handling samples. If a sample produces a noxious odor, try to work with the sample in a hood.

6.2 Preservatives shall not be added to samples before extraction.

6.3 Samples are refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.4 When the waste is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., stored at 4 °C and opened only immediately prior to extraction).

6.5 SPLP extracts should be prepared for analysis and analyzed within the prescribed holding times. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs, in which case samples must be refrigerated at 4 °C. Extracts should be kept at 4 °C for organic non-volatiles analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for VOA analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses and kept at 4 °C.

6.6 Prepared samples (digestates) will be stored for 1 month and then dumped into the disposal drum. When the disposal drum is full, it will be transferred to the chemical management unit for proper disposal.

7.0 EQUIPMENT REQUIRED

7.1 A rotation device that can rotate the extraction vessel end-over-end at 30 ± 2 rpm. The rotation device used by this lab is the 6-vessel, model no. 3740-6, from Associated Design and Manufacturing Co.

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7.2 Extraction vessels for organic non-volatiles must be glass. Plastic extraction vessels can be used if only metallic analytes are required.

The Zero-Headspace Extraction (ZHE) vessel is used when the waste is being tested for the mobility of volatile analytes (VOA). The ZHE vessel allows for liquid/solid separation within the device, and effectively precludes headspace. This vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel. For the ZHE vessel to be acceptable for use, the piston within the vessel should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE vessel is unacceptable for TCLP analyses. The vessel has an internal volume of 500-600 mL, and is equipped to accommodate a 90-110 mm filter. This lab uses a ZHE Model 3745-ZHE, from Associated Design and Manufacturing Co.

The ZHE vessel is used for filtration and shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation, up to 50 psi.

7.3 The filtering device for extractions other than the VOA, can be any device with a minimum internal volume of 300-mL, capable of supporting a 47-mm diameter glass fiber filter, and able to withstand the pressure needed to accomplish separation, up to 50 psi. The filtering device used by this lab is the Millipore Corporation, Model YT30142HW, with a 1500-mL internal volume and requires a 142-mm diameter filter.

7.4 Filters are borosilicate glass fiber, contain no binder materials, and have an effective pore size of 0.6 - 0.8 µm. Glass fiber filters are fragile and should be handled with care. The filters used by this lab for non-VOA extractions are the Whatman, Glass Microfibre Filters - Acid Treated Low Metal, 142 mm, 0.6 - 0.8 µm, cat. no. 1810-142. For VOA extractions, the lab uses Pall Life Sciences, Glass Fiber Filters, 90 mm, 0.7 µm, p/n 66256.

7.5 Glass syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. This lab uses the Model 3775, stainless steel 600-mL gas-tight syringe to collect initial and final filtrates forming the SPLP ZHE extract and to add extraction fluid. A peristaltic pump capable of transferring the extraction fluid into the ZHE vessel without changing the nature of the extraction fluid can also be used.

8.0 REAGENTS

Reagents must not contain detectable analytes of interest. NOTE:All references to water in this method refer to organic-free water from lab NLM-228.

8.1 Sulfuric acid/nitric acid (60/40 weight percent mixture sulfuric/nitric acid.

Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid with stirring in an Erlenmeyer flask standing in an ice bath.

Sulfuric acid (conc)

Sulfuric acid [7664-93-9]

DANGER: Degree of hazard depends upon concentration. Conc. acid mainly refers to those over 52 %.

Handle with care. Wear safety goggles, neoprene gloves and a plastic apron. Use in a hood if mist or fumes generated. Conc. sulfuric acid is a strong, corrosive acid and can cause severe burns. Very carefully add acid to water with frequent or continuous stirring. Mix in a tub or stoppered sink. Upon dilution in water, the generation of heat could cause it to erupt and spatter over a large area. Proceed with caution.
Conc. sulfuric acid is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes and skin.
Inhalation of mist or heated fumes may result in spasm, inflammation and edema of the larynx and bronchi, chemical pneumonitis and pulmonary edema. Symptoms of exposure may include burning sensation or irritation of the nose and throat, coughing, wheezing, laryngitis, shortness of breath, labored breathing, headache, nausea and vomiting.
Avoid skin contact. Conc. acid is extremely corrosive. Symptoms of redness, pain, and severe burn can occur. Circulatory collapse with clammy skin, weak and rapid pulse, shallow respirations, and scanty urine may follow skin contact or ingestion. Circulatory shock is often the immediate cause of death.
Avoid eye contact. Extremely corrosive. Sulfuric acid can cause severe irritation or burns and result in permanent damage. Contact can cause blurred vision, redness, pain and severe tissue burns. Strong concentrations will probably cause blindness.
Long-term exposure may cause erosion of teeth.
Sulfuric acid is an oxidizer and strong dehydrating agent. May cause ignition of finely divided organic materials on contact. Reacts with most metals to produce hydrogen gas, which can form an explosive mixture with air. Keep away from bases, carbides, chlorates, fulminates, nitrates, picrates, cyanides, alkali halides, zinc iodide, permanganates, hydrogen peroxide, azides, perchlorates, nitromethane, phosphorous, nitrites, halogens, metal acetylides, oxides and hydrides, metals (especially finely powdered ones--yields hydrogen gas), strong oxidizing and reducing agents, water, and many other reactive substances.
Reaction products include hydrogen, from reaction with metals, or sulfur oxide fumes when heated.
Permissible exposure limit (PEL) is 1 mg/m^3.
Mist is a known carcinogen, depending on duration and level of exposure.

Nitric acid

Nitric acid (concentrated), HNO_3. CAS # 7697-37-2

DANGER: Handle with care. Wear safety glasses, vinyl gloves, lab coat, and use in a hood. Conc. nitric acid is a strong, corrosive acid and liquid and vapor can cause severe burns. Carefully add acid to water with frequent or continuous stirring. Upon dilution in water, the generation of heat could cause it to erupt and spatter over a large area. Proceed with caution.
Harmful if inhaled and may cause delayed lung injury. If inhaled, can cause severe irritation or burns of mucous membranes and respiratory system, resulting in coughing, difficult breathing, chest pains, pneumonia, pulmonary edema, lung inflammation, unconsciousness, and may be fatal. Can cause severe ulceration.
Skin contact can cause severe irritation, redness, pain, and severe skin burns. Concentrated acid causes deep ulcers and stain skin a yellow or yellow-brown color.
Eye contact can cause severe irritation or burns and result in permanent damage.
Long-term exposure to concentrated vapors may cause erosion of teeth.
Nitric acid is a strong oxidizer. Contact with combustible materials, flammable materials -such as wood and solvents - or powdered metals can cause fire or explosion. Reacts with most metals to produce hydrogen gas, which can form an explosive mixture with air. Keep away from strong bases, carbides, carbonates, charcoal, (hydrogen) sulfides, cyanides, combustible materials, combustible organics or organic materials, turpentine, strong reducing agents, most common metals, carbides, ammonium hydroxide, water, and alcohols.

Certain mixtures with benzene, 1,2-dichloroethane, or dichloromethane may be detonatable. Reaction products include highly toxic and dangerous fumes of reddish oxides of nitrogen having the equivalent affects as those noted above.
Short-term exposure limit (STEL) is 10 mg/m^3 (4 ppm) and permissible exposure limit (PEL) is 5 mg/m^3 (2 ppm).

8.3 Extraction fluid.

8.3.1 Extraction fluid # 1. Add the 60/40 weight percent mixture of sulfuric/nitric acid solution (8.1) to reagent water until the pH is 4.20 ± 0.05. The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River and the leachability of wastes and wastewaters.

NOTE: Solutions are unbuffered and exact pH may not be attained.

8.3.2 Extraction fluid # 2. Add the 60/40 weight percent mixture of sulfuric/nitric acid solution (8.1) to reagent water until the pH is 5.00 ± 0.05. The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

8.3.3 Extraction fluid # 3. Reagent water used to determine cyanide and volatiles leachability.

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extaction fluid prepared.

8.4 Solution preparation

8.4.1 Solutions will be prepared following established recipes located in a solution prep log book. All solution prep will be recorded in a log book, noting any variations to a recipe as needed. If a recipe does not exist, the prep log must state the volume, lot number, and expiration date of the stock solutions used, as well as the final volume and expiration date of the prepared solution.

8.5 Compressed N_2 gas.

9.0 PROCEDURE

Note: All weighing shall be measured to the nearest 0.1 gram.

9.1 Determine the percent solids of the waste that are liquid or multiphasic, liquid/solid. Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure.

9.1.1 Pre-weigh a filter and a container that will receive the filtrate to the nearest 0.001 g. Place the filter in the filtering device.

9.1.2 Weigh a 100-g minimum aliquot of the sample and record the mass. Try to use an amount that will produce 100 g of solids. Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

9.1.3 Transfer the aliquot to the filtering device and spread evenly over the surface of the filter. If filtering the waste at 4 °C will reduce the amount of expressed liquid over what would be

expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If waste material (> 1 % of original sample mass) has adhered to the container used to transfer the sample to the filtration apparatus, determine the mass of this residue and subtract it from the sample mass to determine the actual mass of the sample that will be filtered.

9.1.4 Gradually apply vacuum pressure up to 10 psi and when no additional liquid has passed through the filter in a 2-min interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi, waiting at each 10-psi increment until a 2-min interval in which liquid does pass through the filter is reached. When the flow has ceased for 2 min at 50 psi, stop the filtration. The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

9.1.5 Determine the mass of the liquid phase by subtracting the mass of the filtrate container from the total mass of the filtrate-filled container. Determine the mass of the solid phase of the waste sample by subtracting the mass of the liquid phase from the mass of the total waste sample.

9.1.6 Calculate the percent solids as follows: % solids = mass of solids ÷ sample mass x 100

9.1.7 If the percent solids is ≥ 0.5 %, then proceed to determine whether the solid material requires particle size reduction. If the percent solids is < 0.5 %, then the filtrate is the extract.

9.2 Determine if the solid portion of the waste requires particle size reduction. Particle size reduction is required, unless the solid is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5-mm standard sieve). Reduce the particle size by crushing, cutting, or grinding the waste to a particle size smaller than 1 cm in its narrowest dimension.

If the solids are prepared for organic volatiles extraction, special precautions must be taken. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 °C prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

9.3 Determine the appropriate extraction fluid to use for the non-volatiles extraction as follows:

NOTE: SPLP extraction for volatiles uses only extraction fluid #3.

9.3.1 Aliquot 5.0 g of the solid phase of the waste into a 500-mL beaker.

9.3.2 Add 96.5 mL of DDI-water to the beaker, cover with a watchglass, and stir vigorously for 5 min using a magnetic stirrer.

9.3.3 Measure and record the pH. If the pH is < 5.0, use extraction fluid #1. If the pH is > 5.0, add 3.5 mL 1N nitric acid, slurry briefly, cover with a watchglass, heat to 50 °C and hold for 10 min.

9.3.4 Let the solution cool to room temperature and record the pH. If the pH is < 5.0, use extraction fluid #1. If the pH is > 5.0, use extraction fluid #2.

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9.4 **SPLP extraction procedure when volatiles are not involved.**
A minimum sample size of 100 g (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the percent solids of the waste, whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of SPLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single SPLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

9.4.1 If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100 % solid), aliquot 100 g (minimum). Transfer the aliquot to an appropriate extraction vessel (glass or plastic) and record the sample weight.

If the sample is ≥ 0.5 % solids, liquid/solid separation is required. If enough solid sample was obtained from step 9.1 (determining the percent solids), then use the solid sample for the extraction and refrigerate the liquid portion at 4 °C. If enough solid sample was not obtained from step 9.1, repeat step 9.1 using enough sample to generate enough solid sample. Transfer the aliquot to an appropriate extraction vessel and record the weight of the solid sample (g equivalent solids).

If the sample is < 0.5 % solid, the filtrate is the SPLP extract. Filter enough sample to perform all analyses.

9.4.2 Determine the amount of extraction fluid to add to the extractor vessel as follows:

amount of extraction fluid to add in mL = 20 x weight of g equivalent solids of sample

Slowly add this amount of appropriate extraction fluid to the extraction vessel, close the lid, and secure in the rotation device.

9.4.3 Rotate at 30 ± 2 rpm for 18 ± 2 hr. The temperature of the room in which extraction takes place shall be maintained at 23 ± 2 °C during the extraction period. Record the rpm of the rotation device, the date and time the extraction started, the date and time the extraction stopped, and the minimum and maximum temperature during the extraction.

NOTE: As agitation continues, pressure may build within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate-containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 min, 30 min, and 1 hr) and vented into a hood.

9.4.4 Filter the material in the extractor vessel through a glass fiber filter into a glass container or plastic container if only metals are required. For final filtration of the SPLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration.

If the waste contained no initial liquid phase, the filtrate is defined as the SPLP extract.

If the waste was multiphase and the previous filtered liquid phase is compatible with the filtrate (e.g., multiple phases will not result on combination), combine the liquid and filtrate to form the SPLP extract.

If the initial liquid phase of the waste, is not compatible with the filtrate, analyze these liquids, collectively defined as the SPLP extract, and combine the results mathematically.

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9.4.5 Following the collection of the SPLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots should be acidified with conc. HNO_3 to pH < 2. If precipitation is observed upon addition of HNO_3 to the SPLP extract, refrigerated the SPLP extract at 4 °C and analyze as soon as possible. All other aliquots must be stored under refrigeration at 4 °C until analyzed. The SPLP extract shall be prepared and analyzed according to appropriate analytical methods. SPLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ± 0.5 %), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$$

where:
V1 = volume of the first phase (L)
C1 = concentration of the analyte of concern in the first phase (mg/L)
V2 = volume of the second phase (L)
C2 = concentration of the analyte of concern in the second phase (mg/L)

9.4.6 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations.

9.5 Procedure when volatiles (VOA) are involved.

Use the ZHE device to obtain SPLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.). Sample only once and do not open the device until the final extract (of the solid) has been collected as repeated filling of the ZHE to obtain 25 g of solid is not permitted. Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4 °C) to minimize loss of volatiles.

9.5.1 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample based upon sample size required. Secure the gas inlet/outlet flange (bottom flange) onto the ZHE vessel. Secure the glass fiber filter between (rough side of filter facing sample) the support screens and set aside. Set the liquid inlet/outlet flange (top flange) aside.

9.5.2 If the waste is 100 % solid, aliquot a 25-g maximum, transfer to the ZHE vessel, and record the weight.

If the waste is ≥ 0.5 % solids, use the percent solids information to aliquot up to 25 g equivalent solids into the ZHE vessel and record the weight. Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

$$\text{mass of waste to charge filter (g)} = 25 \div \%\ \text{solids} \times 100$$

If the sample has a percent solids < 0.5 %, the filtrate is the SPLP extract. Fill the ZHE vessel with enough sample to filter to perform all the analyses.
Transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom).

NOTE: If waste material (> 1 % of original sample mass) has obviously adhered to the container used to transfer the sample to the ZHE, determine the mass of this residue and subtract it from the sample mass to determine the mass of the waste sample that will be extracted.

9.5.3 Attach a gas line to the gas inlet/outlet valve (bottom flange), and with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure up to 10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood.

If the waste is 100 % solid, slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device.

For a multiphase sample, at the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. Attach the stainless steel syringe to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure up to 10 psi to force the liquid phase of the sample into the filtrate collection container. When no additional liquid has passed through the filter in a 2-min interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi, waiting at each 10-psi increment until a 2-min interval in which liquid does pass through the filter is reached. When liquid flow has ceased for 2 min at 50 psi, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, disconnect, and weigh the filtrate into a VOA vial. The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the SPLP extraction as a solid.

The liquid phase may now be either analyzed immediately or stored at 4 °C under minimal headspace conditions until time of analysis.

9.5.4 Determine the volume of extraction fluid #1 to add to the ZHE as follows:

amount of extraction fluid to add in mL = 20 x weight of g equivalent solids of sample

Add the appropriate amount of extraction fluid to the ZHE vessel through the liquid inlet/outlet using a syringe or pump. After the extraction fluid has been added, immediately close the liquid inlet/outlet valve.

9.5.5 Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 35 - 70 kPa (5-10 psi). In a hood, slowly open the liquid inlet/outlet valve to bleed out any headspace that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at

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the first appearance of liquid from the valve. Re-pressurize the ZHE with 35 - 70 kPa (5-10 psi) and check all ZHE fittings to ensure that they are closed.

9.5.6 Place the ZHE in the rotary agitation apparatus and rotate at 30 ± 2 rpm for 18 ± 2 hr. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 22 ± 3 °C during agitation. Record the time and temperature on the data sheets.

9.5.7 Following the 18 ± 2 hr agitation period, check the pressure of the ZHE. If the pressure has not been maintained, perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the extract is filtered through the glass fiber filter, using the ZHE device as discussed in part 9.5.3.

NOTE: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

NOTE: All extract will be filtered.

If the waste contained an initial liquid phase, the extract is filtered into a separate filtrate collection container from the initial liquid phase of the waste. The initial filtrate is identified as Z1 and the final filtered extract as Z2. Z1 and Z2 are collectively defined as the SPLP extract.

If the original waste contained no initial liquid phase, the ZHE filtrate defined as the SPLP extract.

9.5.8 Following collection of the SPLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4°C until analyzed. Analyze the SPLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final Analyte Concentration} = \frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$$

where:
V1 = volume of the first phase (L)
C1 = concentration of the analyte of concern in the first phase (mg/L)
V2 = volume of the second phase (L)
C2 = concentration of the analyte of concern in the second phase (mg/L)

9.5.9 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations.

10.0 QUALITY CONTROL

10.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel. For samples that are < 0.5 % solids and are filtered only, filter an equivalent amount of extraction fluid # 1 for use as a SPLP blank.

10.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment sludge, contaminated soil, etc.) unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. A minimum of one matrix spike must be analyzed for each analytical batch. Matrix spikes are to be added after filtration of the SPLP extract and before preservation. In most cases, matrix spikes should

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be added at a concentration equivalent to the corresponding regulatory level (at a minimum of 5 × MDL). The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. The bias determined from the matrix spike determination shall **NOT** be used to correct the measured values.

The % matrix spike (MS) recovery is calculated by the following formula:

% MS recovery = ((spike result - sample result) ÷ spike added) × 100

10.3 All quality control measures described in the appropriate analytical methods shall be followed.

10.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if:

(1) Recovery of the contaminant from the SPLP extract is not at least 50 % and the concentration does not exceed the regulatory level

and

(2) The concentration of the contaminant measured in the extract is within 20 % of the appropriate regulatory level.

10.4.1 The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

10.4.2 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The fourth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50 % of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100 % and 150 % of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrumental technique. All four aliquots are analyzed.

10.4.3 Subject data to linear regression of instrumental signals as the dependent variable (y-axis) versus concentrations of the additions of standard as the dependent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

10.4.4 Alternately, subtract the instrumental signal of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Subject data to linear regression of the corrected instrument signals as the dependent variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

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10.5 Samples must undergo SPLP extraction within the following time periods:

Sample Maximum Holding Times (days)

	From: field collection to: SPLP extraction	From: SPLP extraction to: preparative extraction	From: preparative extraction to: determinative analysis	Total elapsed time
Volatiles	14	NA	14	28
Semivolatiles	14	7	40	61
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

11.0 KEY WORDS

40 CFR 261, Method 1312, SW846, SPLP, Synthetic Precipitation Leaching Procedure, ZHE, Zero Headspace Extraction

12.0 REFERENCES

12.1 USEPA, SW846, EPA Method-1312, Revised September, 1994.

12.2 Code of Federal Regulations, 40 CFR 261, July 1992, revision 0.

13.0 REVISION HISTORY

13.1 The method was updated on 06/01/09 to be more lab specific, to reflect the current SOP format, and to include additional safety information.

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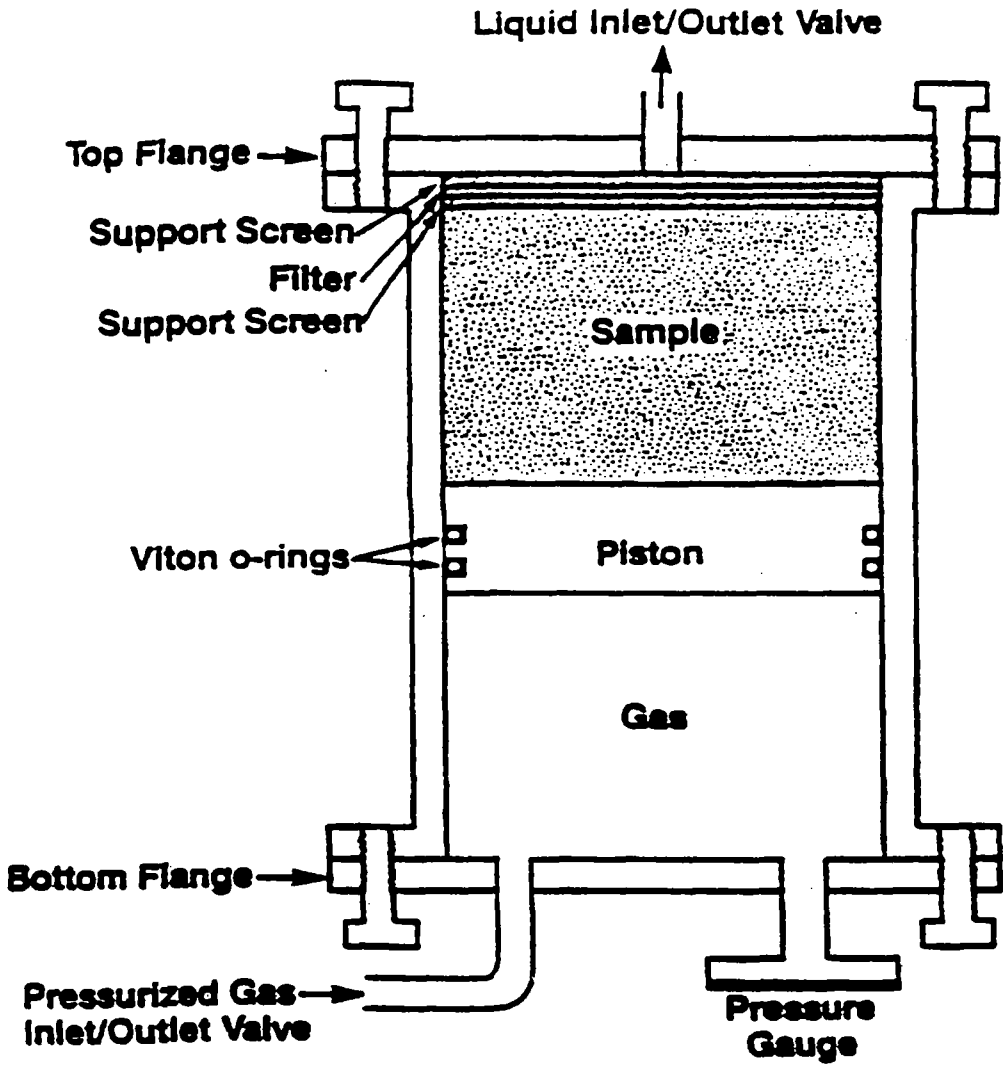

Figure 1. Zero-Headspace Extractor (ZHE)

TABLE 1
VOLATILE ANALYTES[1]

Compound	CAS No.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1]When testing for any or all of these analytes, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

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Hardness by Calculation

Process Owner (TS/PM/OM/LM)	Not valid without colored "Controlled" stamp (unless printing date appears)
Dan Deprez	Valid one calendar day from (supports **OQ O-Proc Writ** reviewed August 2007) , expires at midnight. (Also valid for the process' duration.)
Assignment	Reviewed May 29, 2009 by Christine Devine
Electronic only unless colored "Controlled" stamp is present	

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1.0 SCOPE

This method is used to calculate hardness in mg equivalent $CaCO_3$/L using calcium (Ca) and magnesium (Mg) results in mg/L. This method is equivalent to Standard Methods 2340 B Hardness by Calculation (18th Edition, 1992).

2.0 SUMMARY OF METHOD

The concentration of calcium and magnesium in mg/L of a sample are determined using an ICP or ICPMS. Hardness of the sample is calculated in mg equivalent $CaCO_3$/L.

3.0 CALCULATION PROCEDURE

Hardness, mg equivalent $CaCO_3$/L = 2.497 × [Ca, mg/L] + 4.118 × [Mg, mg/L]

4.0 KEY WORDS

Ca, Calcium, Hardness Calculation, Magnesium, Mg

5.0 REFERENCES

Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992, Method 2340 B.

6.0 REVISION HISTORY

5/28/09-No changes needed.

STANDARD OPERATING PROCEDURE

for

SAMPLE TRACKING AND INTERNAL CHAIN-OF-CUSTODY

SOP No.: SMO-SCOC

UNCONTROLLED

Revision: 12

April 23, 2009

Approved By: _____ Supervisor — 4/24/09 Date

_____ QA Manager — 4/24/09 Date

COPY

_____ Laboratory Manager — 4/27/09 Date

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Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL

NUMBER: _____

Initials: _____ Date: _____

SAMPLE TRACKING AND INTERNAL CHAIN-OF-CUSTODY

1. PURPOSE

The purpose of this procedure is to maintain and document internal chain-of-custody (COC) of samples. Custody documentation must be maintained through all phases of analysis - from sample receipt and initial storage to analysis and disposal.

2. APPLICABILITY

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The procedure is applicable to all field samples, subsamples, and sample extracts and sample digestates as described in the procedure section.

3. DEFINITIONS

3.1. Custody - The guardianship or safe keeping of a sample. A sample is considered to be in a person's custody if it is physically in their possession, or it is in their view after being in their possession, or it was in their possession and then locked up or sealed to prevent tampering, or it is in a secure area.

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3.2. Chain of Custody - The documented order or sequence of the persons having custody of a sample. Chain of custody requires that the sample be in custody of some known person from the time it is collected until it is disposed.

3.3. Custody record - External or internal COC document that clearly defines and documents who is/was in possession of a sample at a given time.

3.4. Login - The SMO process of accepting the sample, inspecting, and entering the sample information into the laboratory LIMS system.

3.5. Sample custodian – The sample management office (SMO) is considered to be the sample custodian for any period of time from sample receipt to sample disposal that the sample is not internally signed into custody by analytical personnel.

3.6. Sample tracking - Identifying or reproducing the path of sample custody throughout the laboratory.

4. DISCUSSION

Chain of custody is the protocol that provides a record of the persons having control of and access to a sample. If the analytical results are questioned the chain of custody documentation is the record that proves the sample was collected and handled according to specification and the sample can be directly linked to the analytical results. This is especially important if the analytical results are questioned or to be used in supporting legal proceedings.

5. RESPONSIBILITIES

5.1 It is the responsibility of sample custodians and laboratory staff to make sure that the procedures described in this SOP are followed and that chain of custody records are complete and accurate. Every appropriate laboratory staff member will be required to familiarize themselves with the procedures listed in this SOP. Once the SOP has been read, appropriate supervisory personnel and section managers must ensure that personnel will comply with the procedures listed herein.

5.1.1. **Sample Custodian Responsibilities:** It is the responsibility of the Sample Custodian to fill sample requests by the time indicated by the analyst. Once the samples are gathered SMO will transfer custody and deliver the samples directly to the requestor. Upon return of the samples (within designated business hours) from the analyst, it is the responsibility of SMO to scan the samples back into their home storage location and re-shelve them. Samples returned after hours the previous day are to be shelved to their designated shelves by the sample custodians.

5.1.2. **Analyst Responsibilities:** It is the responsibility of the analyst to provide sufficient time for sample requests to be filled by the Sample Custodians. It is the responsibility of the analyst to take custody in the LIMS system as soon as they take samples from a storage location. Upon completing their work, samples must be returned to the sample storage room as soon as possible to minimize the amount of time samples are held at room temperature.

6. PROCEDURES

6.1. Field sample custody

6.1.1. Sample containers are labeled with a bar-code to identify, and track field samples throughout the laboratory. The bar-coding system uses CAS LIMS database for sample information. The sample tracking process in the laboratory begins with receipt of samples into the laboratory facility. Sample receipt, login, identification, labeling, and storage procedures are all described in the SOP SMO-GEN *Sample Receiving*. Sample receiving personnel will enter the sample information (Service Request number, unique container ID) for each project into the sample database. Following login, the samples are placed in the appropriate refrigerator(s).

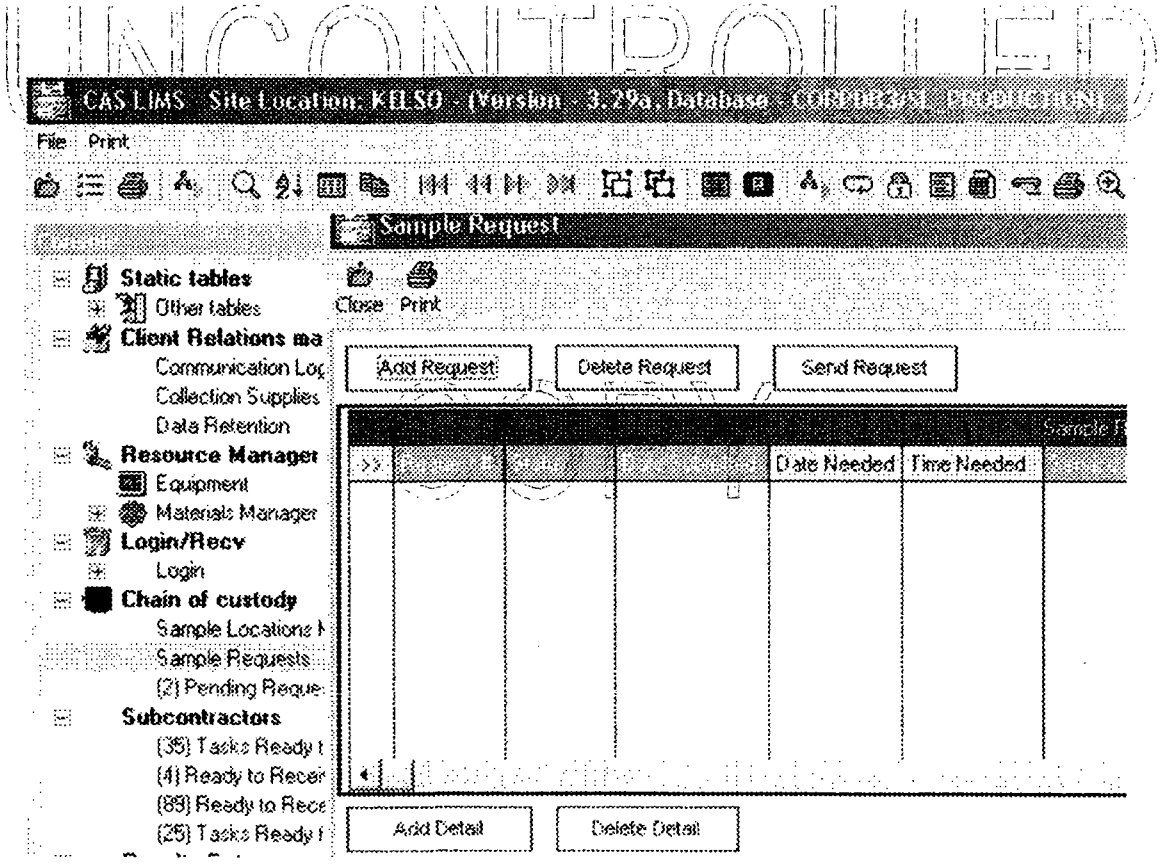
6.1.2. Access to all samples is controlled. Samples are stored in a secure, keypad-locked room or in separate locked storage areas. While in these secured and locked storage

areas, the samples are considered to be in the custody of the sample management office (sample custodian). Removal of any sample from the SMO sample storage areas represents a physical change of custody and therefore must be documented via a chain of custody record. It is at this point that internal tracking of the samples is initiated.

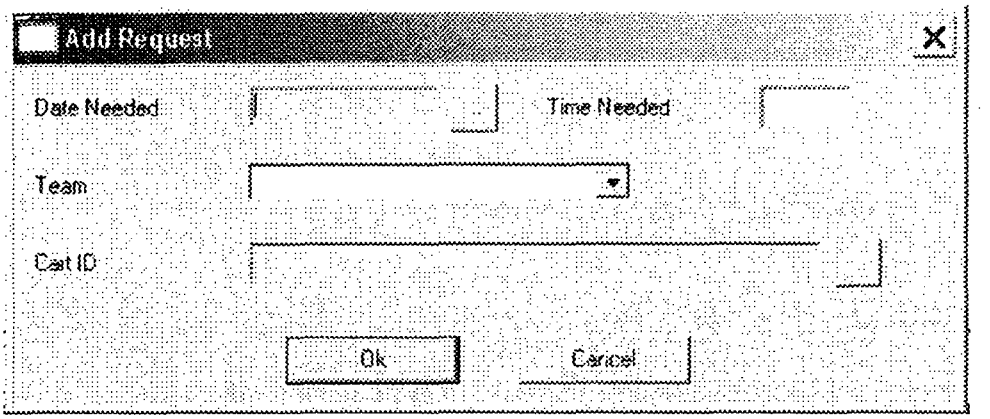
Note: All solid samples pulled from a freezer must be placed in a Ziploc storage bag to prevent loss of sample in the event that the jar cracks during thawing.

6.2. Requesting Samples through the Sample Custodian

6.2.1. Open the sample request window by clicking on "Sample Requests" under the "Chain of Custody" heading. Click the "Add Request" button.



6.2.2. Enter the necessary information in the Add Request window and click OK.



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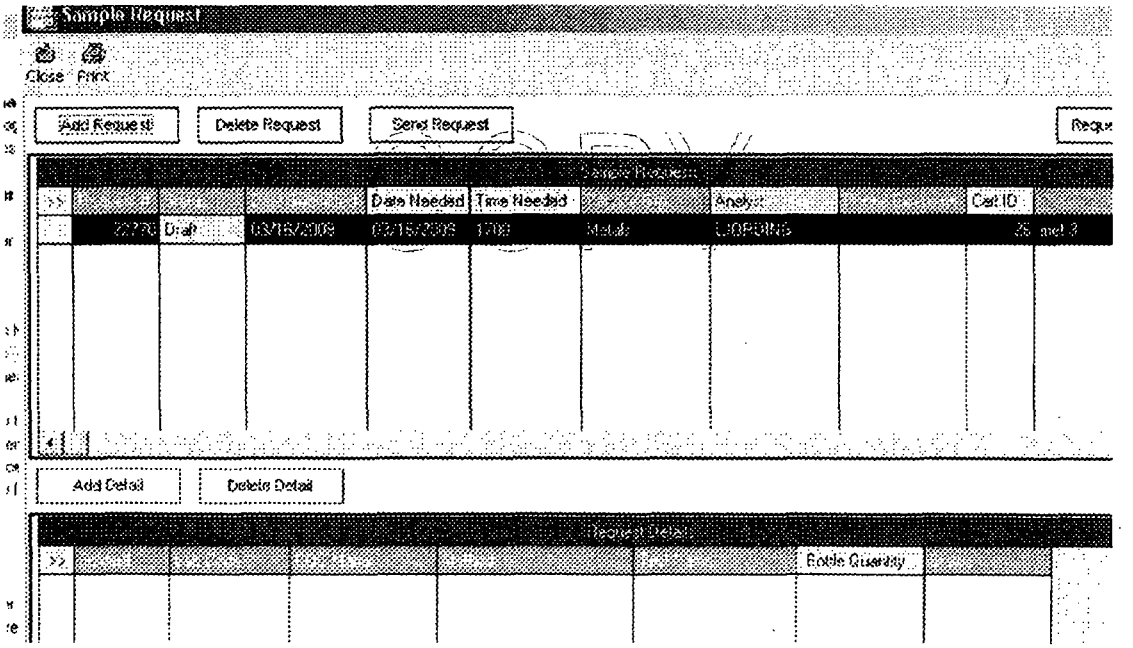
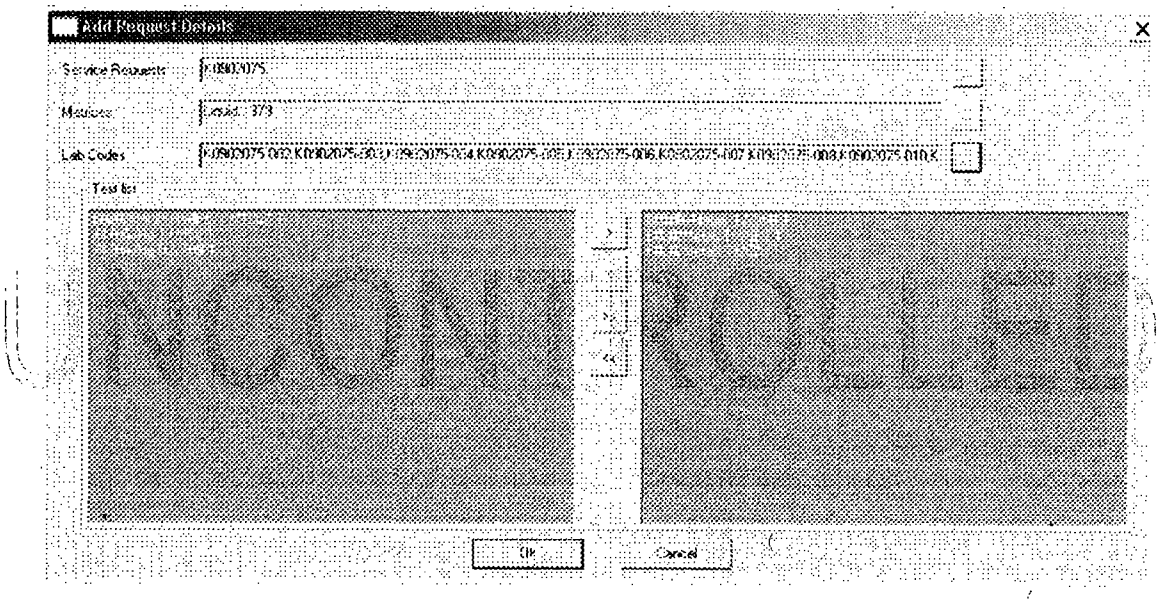
6.2.3. The sample request screen will appear with the basic information as seen below. To add samples to the request click on the "Add Detail" button.

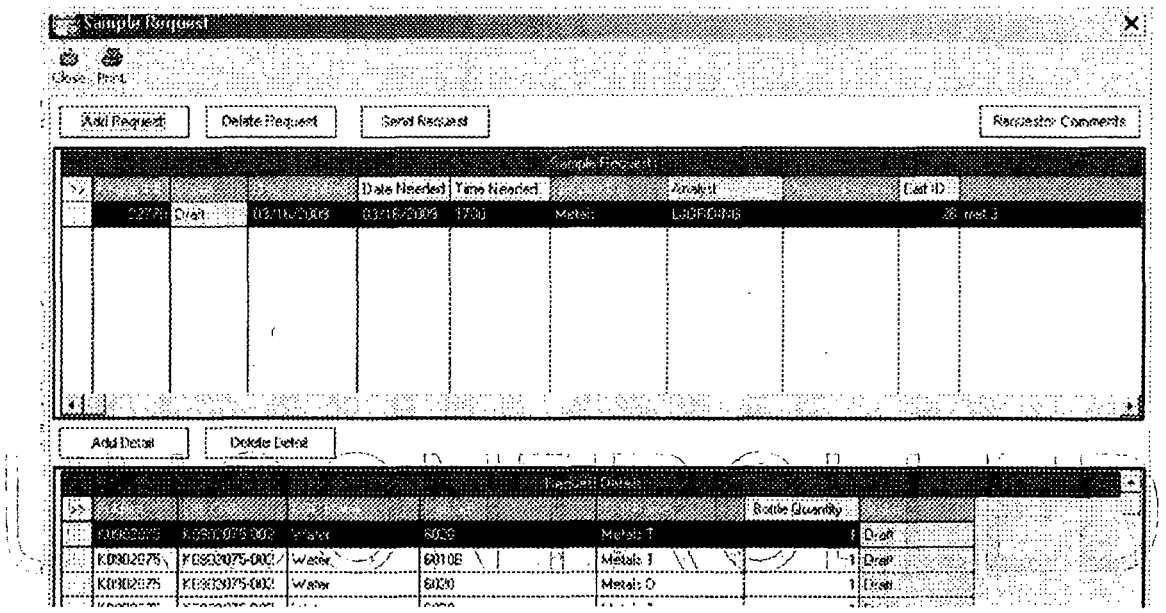


6.2.4. Fill in the details (Service Requests, Matrices, Lab Codes) and select the tests by highlighting and moving them to the right in the Test List box. Click OK.



6.2.5. Once all of the samples have been added to the sample request, add any additional information to the request in the "Requestor Comments" field. (Additional information may include things like specific containers needed, extra volume necessary for QC on a given sample, etc.) Once the request is complete click the "Send Request" button.

Note: If one of your team members will be taking possession of the samples (i.e. a swing shift team member completes the sample request form but a day crew person will be taking custody of them to begin the testing) double click on the "analyst" field and change it to the person to whom the samples should be delivered and custody given to.



6.3. The steps to be taken to by SMO to fill a sample request.

6.3.1. Under Chain of Custody open up the Pending Requests folder and double click the request. The following screen will appear showing the requested list of samples, who requested them, and the date and time they are needed. Print the request and retrieve the necessary samples.

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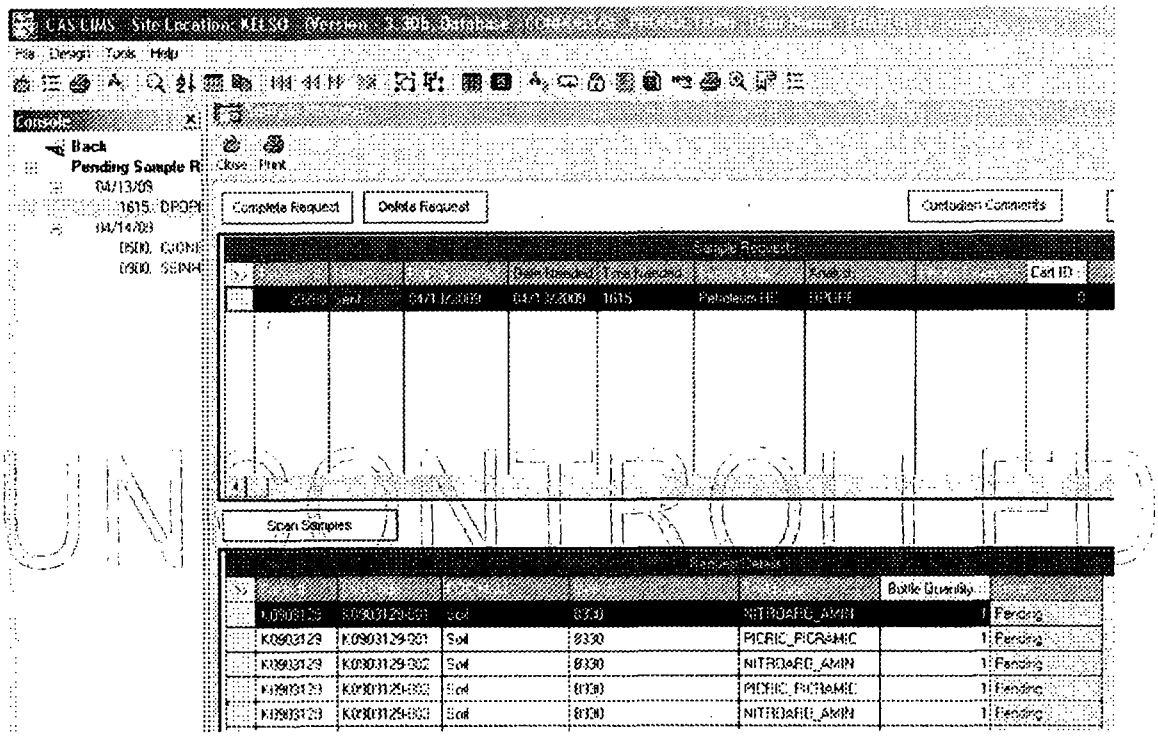
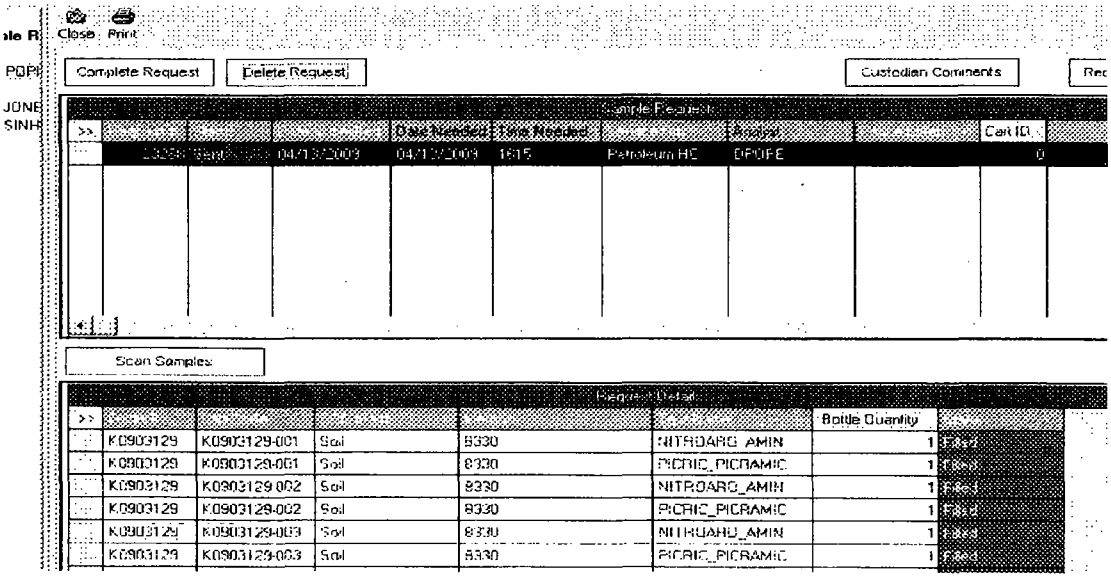
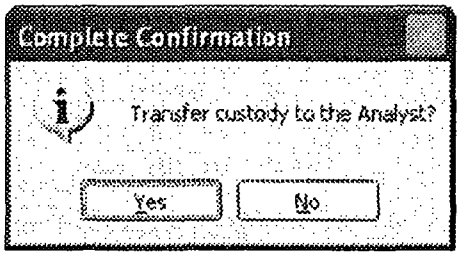


6.3.2. Click on the Scan Samples button and scan each individual bottle. When all bottles are scanned in click the cancel button. Review the order to see if any bottles were missed. If the samples are not ready to be delivered do not complete the order. Place the order in the appropriate refrigerator for delivery at the appropriate time. If the order is ready to go to the analyst, complete the order by clicking the "complete request" button and click "Yes".



6.3.3. To finish the order and transfer the custody to the requesting analyst, click "Yes".



6.3.4. Deliver the samples to the analyst who now has custody of them.

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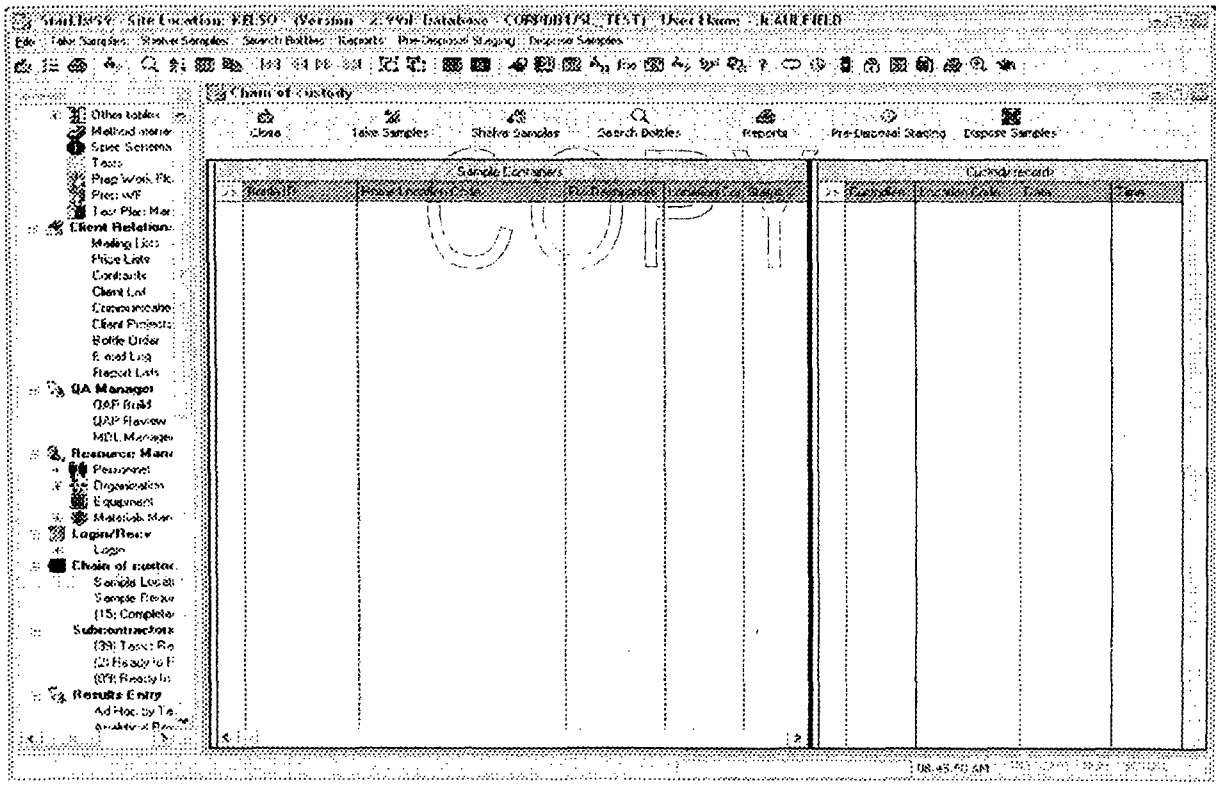
6.4. The steps to be taken to take custody of samples retrieved by an analyst are outlined below:

6.4.1. The main menu display on the internal custody workstation appears as follows:



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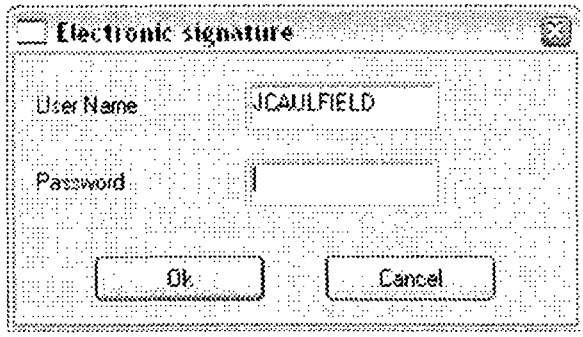
6.4.2. Choose Take Samples. The following Signature window will appear:



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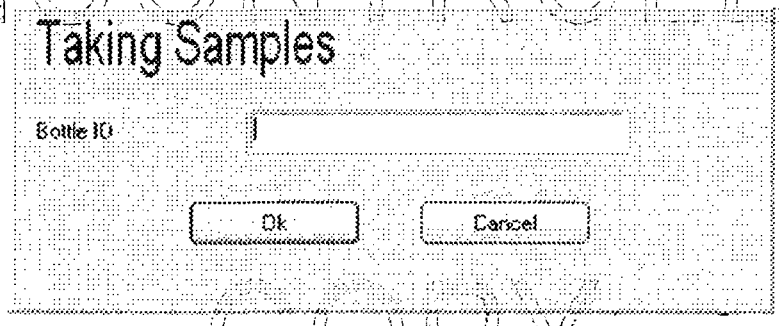
6.4.3. Select name from employee list. The Taking Samples screen will appear next.



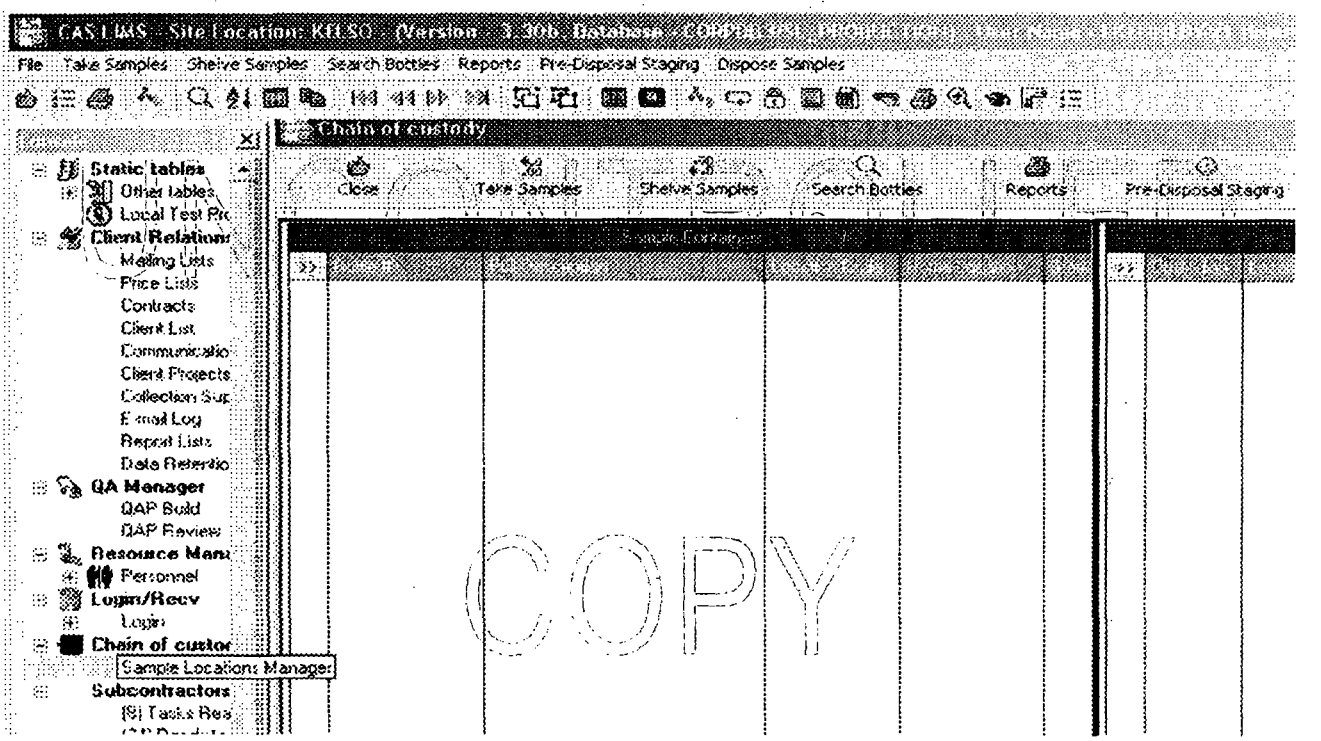
6.4.4. Using the barcode reader, read the barcode for each sample to be removed and taken into custody. The sample list will appear in the window displayed. It is recommended that a brief comparison of the displayed list and the actual container IDs be made.

6.5. Returning samples

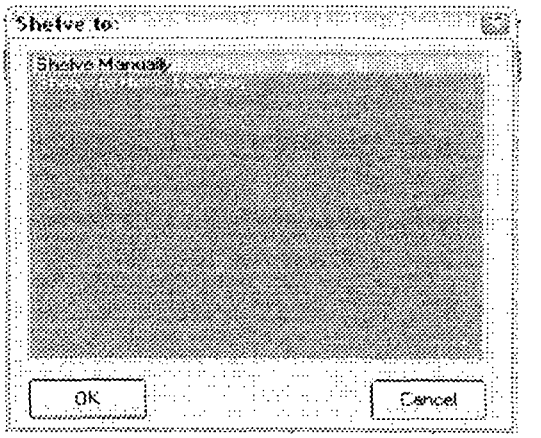
6.5.1. When the analyst is finished working with the samples, the samples are returned to the main storage room and checked back in to complete the custody record. If the samples are returned during business hours or when a sample custodian is on duty, the sample can be left in the designated return area and SMO will scan and shelve the samples to the home location. If the samples are being returned after hours our outside the schedule of the sample custodians, the analyst must scan the samples to the appropriate designation "Cart in Delilah" or "Cart in Herk" etc. and place the samples, or sample cart, in the designated refrigerator(Sec 6.5.2). SMO will retrieve and scan them to their home location and shelve them the next business day. No samples other than room temperature samples can be left outside the refrigerator.

NOTE: Foreign soil samples or VOA samples must be scanned to their home location and placed in the proper refrigerator and shelf by the analysts or sample custodian. These samples must never be placed in a refrigerator outside of the one to which they are assigned.

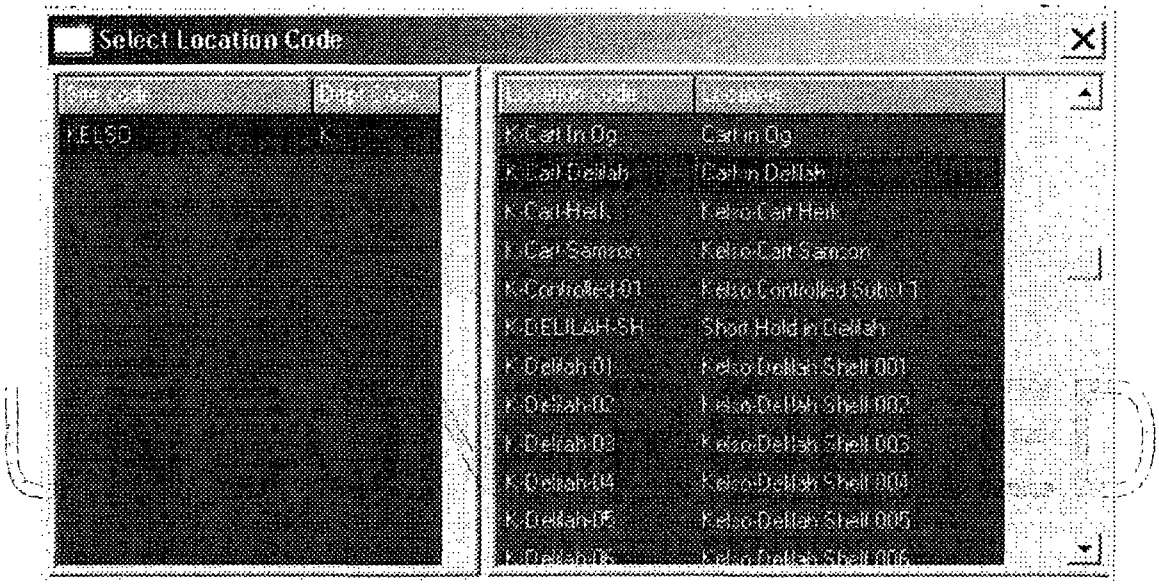
6.5.2. To return samples after hours or outside SMO hours: Choose Sample Location Manager from the Chain of Custody tab and click the shelve samples button.



6.5.3. Choose "Shelve Manually" and click OK.



6.5.4. Choose the sample location (i.e. Cart in Delilah, Cart in Herk, etc.) by double clicking.



6.5.5. Scan each sample container. DO NOT check the Empty checkbox even if the container is empty. Empty containers can be left on a cart outside the refrigerator and do not need to be scanned in.

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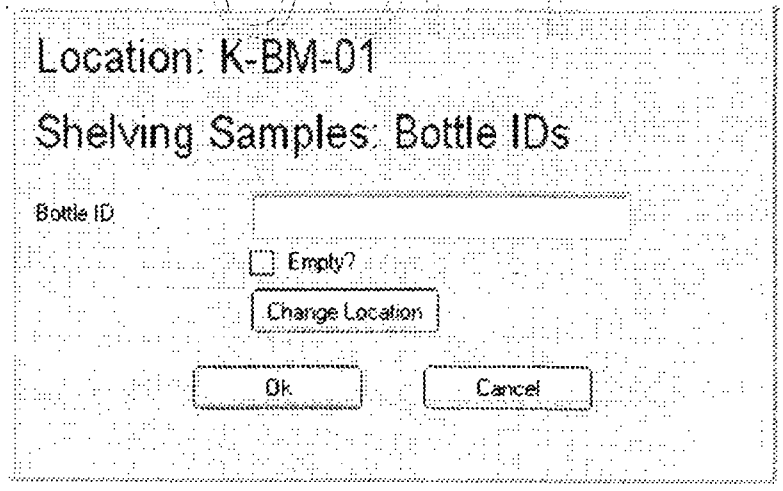

6.6. Sample tracking

6.6.1. Sample custody can be tracked via the Search function. Using this function, an analyst looking for a container that is in another analyst's custody can locate the container. The function is also used to document all custody events and provide internal chain of custody history. At the main menu window, choose Search Bottles. The Search window will appear.

6.6.2. The search can be done several ways by choosing one of the criteria in the Search Criteria window. The window will appear with all custody information.

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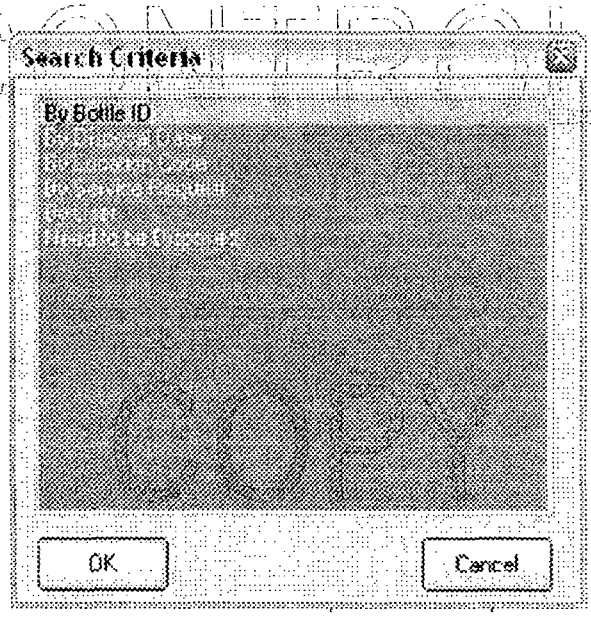


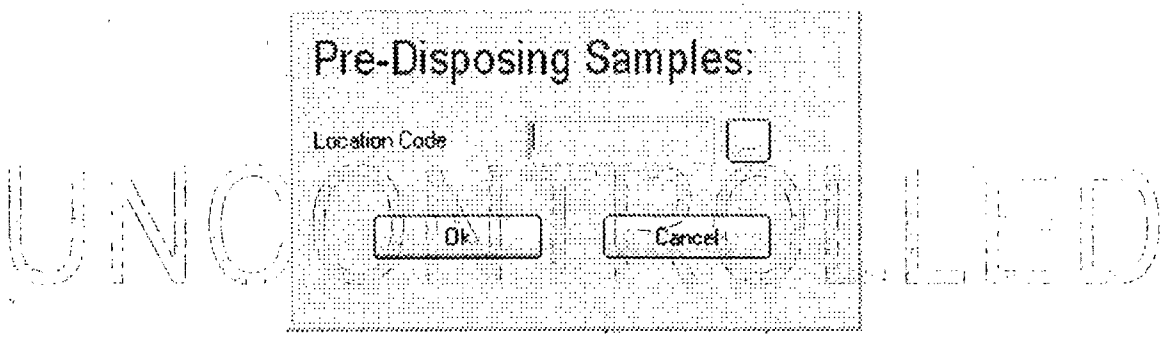
6.7. Custody of extracts and digestates

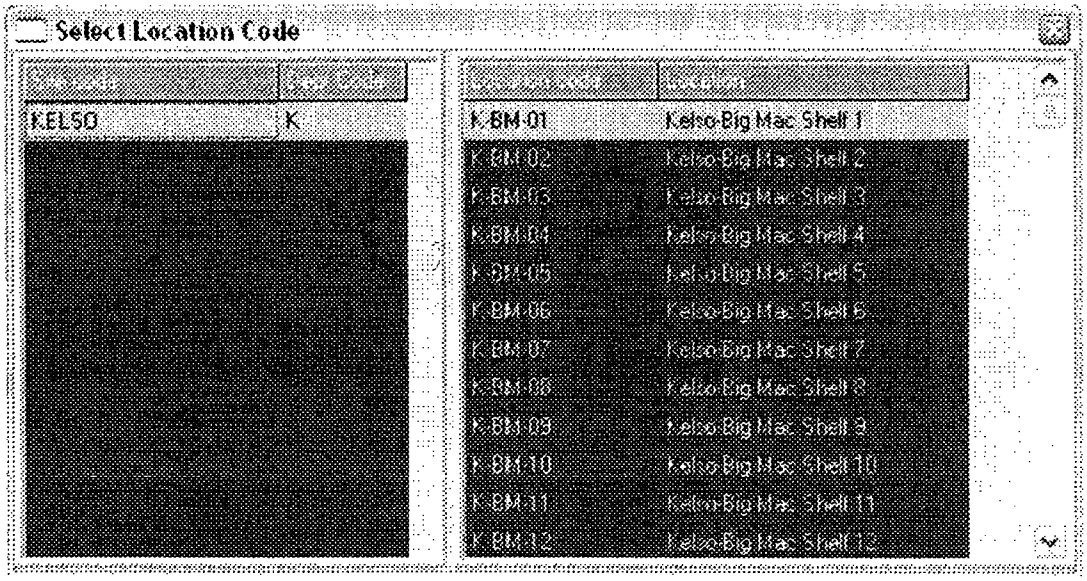
6.7.1. In labs where separate analysts prepare samples (extraction or digestion) for instrument analysis, the transfer of custody of completed extracts or digestates is documented. The instrument lab analyst accepts custody of the sample extract or digestate by signing on the benchsheet, or similar custody record, that they have accepted custody of those specific extracts or digestates listed. The date and time must accompany the signature.

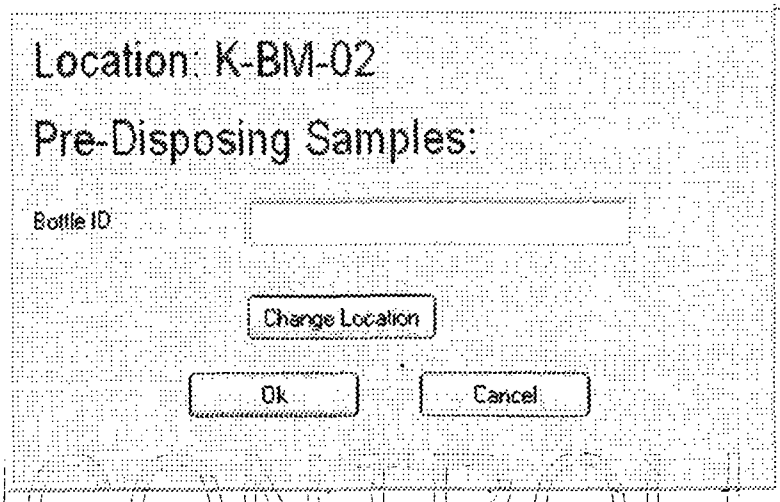
6.7.2. For TCLP extracts, the finished extracts are labeled and logged into the LIMS system as a new container for the sample. The extracts are then stored as with other samples. Custody and tracking is then performed as for field samples as discussed in sections 6.1 and 6.2.

6.8. Pre-Disposal of Samples

6.8.1. When the analytical report has been shipped to the client, the sample containers are removed from refrigeration and placed on pre-disposal holding shelves while still in the custody of SMO. The shelves are referenced in order to facilitate retrieval of a sample if necessary. Transfer is documented using the Pre-Disposal and Location Selection windows.







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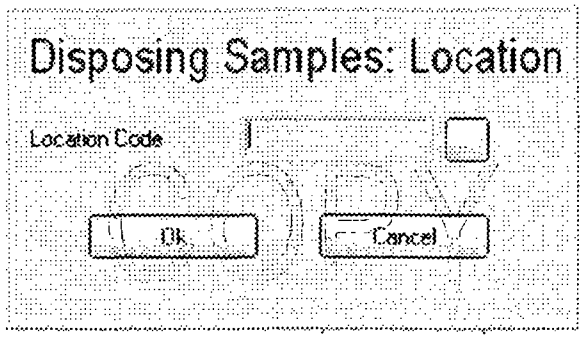
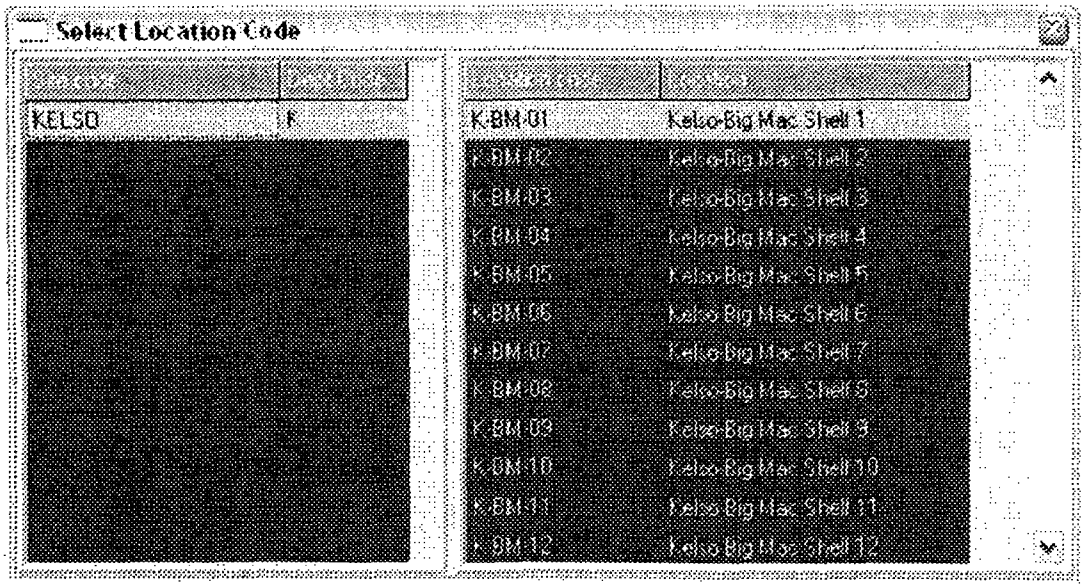
6.9. When sample disposal is performed, each container is scanned. Thus, the endpoint of CAS custody is documented by the final scan and documented disposal date (refer to the SOP SMO-SDIS *Sample Disposal*).





7. RECORDS AND REPORTS

7.1: Each service request will contain one or more references to the location of all of the associated sample containers. The record of hazardous/non-hazardous sample determination is kept in the original service request file.

7.2. After analyses are completed for the entire Service Request and the data is reported, the entire sample custody record is printed and placed in the original SR file. This, and other available reports, is found in the report selection window.

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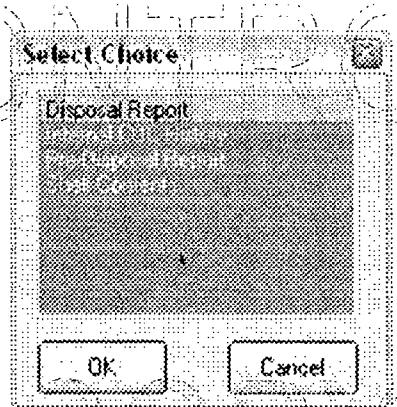

7.3. Human resources and QA records are used to associate the analyst's initials to their actual handwritten signature. The database of internal custody records will be maintained for 5 years. Normal CAS procedures for electronic backup are used.

8. CHANGES SINCE THE LAST REVISION

8.1. Sec 4 Re-wrote to make more current.
8.2. Sec 5.1 Added sample custodian and analyst responsibilities.
8.3. Removed old section 6.1.3. Employee unique barcode ID.
8.4. Sec 6.1.1 Changed lims reference from Access to CAS LIMS
8.5. Sec 6.2 Added this section on how to request samples
8.6. Sec 6.3 How to fill a sample request
8.7. Sec 6.5 How to return samples

STANDARD OPERATING PROCEDURE

SAMPLE RECEIVING

SMO-GEN

Revision 25

April 9, 2009

UNCONTROLLED

Approved By: _____ Supervisor — 4/13/09 Date

_____ QA Manager — 4/13/09 Date

_____ Laboratory Manager — 4/13/09 Date

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COLUMBIA ANALYTICAL SERVICES, INC.
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Kelso, Washington 98626

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Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL
NUMBER: _____
Initials: _____ Date: _____

SAMPLE RECEIVING

1. PURPOSE

This procedure is used to facilitate the correct and expedient receipt, login, and storage of all samples received at CAS.

2. SCOPE AND APPLICATION

This procedure applies to all samples received at CAS. This procedure applies to all phases of sample handling once received, including checking and documentation of sample condition, documenting sample custody, sample login into the Laboratory Information Management System (LIMS), storage, shipping, and disposal

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3. RESPONSIBILITIES

3.1 It is the responsibility of all lab staff who handles samples to adhere to this procedure and to complete all documentation required. It is the responsibility of the department supervisor/manager to ensure that SMO staff is trained on this procedure and that training documentation is available. It is also the responsibility of the SMO supervisor to ensure that a secondary review of all sample login documentation is performed.

3.2 It is the responsibility of all CAS employees to ensure the confidentiality of client information. All information, such as customer name and project information, data, and reports is treated as confidential and is to be kept out of sight of other customers. No information may be given to third parties without the consent of the client.

4. DISCUSSION

4.1 The quality of analytical results is highly dependent upon the quality of the procedures used to collect and handle, and store samples. Therefore, sample management is a critical component of the laboratory operation. This procedure ensures that samples are properly received and logged into the Laboratory Information Management System (LIMS), and that all associated documentation, including chain of custody forms, is complete and consistent with the samples received. Complete documentation of all sample storage is maintained in order to preserve the integrity of the samples and to establish a record of sample handling. All potential problems with a sample shipment are addressed by contacting the client and discussing the pertinent issues.

4.2 During the log-in process, each sample is given a unique laboratory code and a service request form is generated. The service request contains client information, sample

descriptions, sample matrix information, required analyses, sample collection dates, analysis due dates and other pertinent information.

5. PROCEDURE

5.1 Sample receipt, unpacking, and inspection

5.1.1 Upon receipt, sample shipping containers are examined for presence and condition of custody seals, locks, shipping bills, etc. Before processing, all shipping containers (coolers) are initially opened in the hood. The cooler is quickly inspected for any existing hazards such as broken bottles and a thermometer is inserted. The CAS Cooler Receipt and Preservation Form (CRF - see Appendix) is used for the next steps. CAS follows EPA guidelines for preservation and holding time as outlined in the CAS *Quality Assurance Manual* Table 8-1.

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NOTE: If the cooler or any sample exhibits a strong odor, or there is any indication of highly contaminated samples, immediately transfer the cooler/samples to the hood if not already opened there. Ensure that appropriate protective equipment is being used (lab coat, gloves, eye protection, respirator if necessary, etc.). Continue to unpack the cooler. Leave the samples under the hood with the hood running. Notify the Project Chemist of the sample condition. For waste or product samples, store the samples in the hood in SMO. For other samples (water, soil/solid, etc) store the samples in the walk-in cooler(s). If any of the suspect or highly contaminated samples are designated for VOA analysis, DO NOT store with the other VOA samples in the VOA sample refrigerator. Discuss storage options with the Project Chemist and document the storage area/conditions.

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5.1.2 After opening shipping containers, Chain of Custody (COC) forms and any other documents are located removed, and checked for the presence of short holding time or rush samples. The temperatures of the coolers are measured following the guidelines in section 5.4 of this SOP. The acceptance criterion for properly chilled samples in a cooler is 4 $\pm$ 2°C. If a cooler exhibits a temperature outside of the acceptance range, or exhibits any other anomalies, the CRF is attached to the Service Request and submitted for review to the appropriate project manager. Samples or coolers which are received outside of the temperature range are noted on the cooler receipt form.

NOTE: EPA drinking water requirements for microbiology samples (surface water treatment rule and coliphage samples) require that samples be at 10°C or less. If the temperature is > 10°C, the sample results must be flagged by recording the temperature in the "Remarks" section of the Bacteriological

Analysis Form, or by noting the temperature and flagging requirement on the CRF if the results will be reported on standard forms.

NOTE: Some states or projects may require specific cooling requirements for shipping coolers and special cooler temperature assessment procedures. For example, Wisconsin DNR does not allow the use of blue ice.

5.1.3 Rush requests and samples with short holding times are given priority for initial processing. For samples with extremely limited time remaining before the expiration of the holding time and that are in danger of expiring prior to being able to complete the login process, see 5.1.4.2. Sample containers are removed and organized according to chain of custody identification and analysis. Once unloaded, all SMO staff will finish the login and issuing process for short holding time and rush samples prior to working on the remaining samples. Any containers that are received in broken condition or leaking are documented on the Cooler receipt Form (CRF) and on the chain of custody. The appropriate Project Chemist is also notified. For EPA samples which exhibit discrepancies or are damaged upon receipt, the EPA Project Chemist is responsible to notify EPA SMO for direction.

Note: Samples received for NCASI Method WP-99.02 must be kept refrigerated or iced in accordance with section 6.3 of the method SOP. Once the samples are identified and verified against the COC, the samples must be placed back in an iced cooler or a refrigerator until login is complete and samples can be relocated to their assigned storage location. **DO NOT DELIVER SAMPLES TO THE LABORATORY**.

5.1.4 Samples received with short or expiring holding times will be issued via a "Temporary Service Request", prior to the final Project Chemist review, enabling the laboratory to quickly access or process the samples. For samples that require wastewater microbiology testing, the analysis is to begin as soon as possible after receipt at the laboratory. Holding times are assigned according to the sample type, test method, and as prescribed in Standard Methods. Microbiology samples received past the holding time do not meet sample acceptance requirements and a notation is made on the Bacteriological Analysis Form and/or Cooler Receipt and Preservation Form. Decisions regarding the disposition of the samples that do not meet sample acceptance criteria are to be documented on the Cooler Receipt and Preservation Form by the Project Chemist.

5.1.4.1 Sample receiving notifies the laboratory of short hold time samples by creating a copy of the service request for each department and stamping with "Temporary". The original service request is stamped with the "Temporary

Service Request/Custody" stamp for signature of receipt by all receiving labs. The appropriate bottles associated with the short hold samples are scanned to either the department (if bottles need to be delivered to the lab) or to the appropriate home location.

NOTE: Samples received for General chemistry with holding times expiring *before* 10am the following day are to be delivered to the laboratory for analysis. All other samples (excluding VOA & foreign soils) are to be scanned to the Short Hold shelf and delivered to that location for easy retrieval by the analyst. VOA and foreign soils are to be scanned to their home location and placed in the appropriate storage areas.

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5.1.4.2 If the holding time is limited and in danger of expiring prior to the completion of the login process, immediately notify the appropriate laboratory via phoning the department or via over-head paging. When notifying the department, indicate the test and the time the holding time is expiring. Immediately notify the appropriate PC via phoning them or via over-head paging. Complete the cooler receipt form noting any discrepancies. Create two copies of the Chain of Custody and stamp one with the "Custody Transfer" stamp. This copy is to remain in SMO. When samples are removed from SMO the chemist signs for custody of the sample(s) noting the time taken. A copy of the COC is made available to the analyst. Analysts must return the original sample to SMO as soon as possible so that the login and labeling process can be completed. Upon returning the sample, the analyst relinquishes custody back to SMO by signing the COC and noting the time returned. SMO takes custody by signing the COC and noting the time.

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5.1.5 For water VOA samples (those received in 40mL VOA vials), inspect the vials for headspace.

5.1.6 Listed below are items which must be verified against the chain of custody information as it applies to samples and containers received:

- Sample identification
- Number of containers received
- Matrix
- Correct bottles for analysis requested.
- Correct/sufficient sample volume for analysis
- Correct preservatives for analysis. The CAS sample bottle preparation form is attached as a reference for proper preservatives.

At this point, a brief evaluation of the amount of sample provided for the requested analyses is made. Compare the sample containers and estimated amount of sample provided to the analyses requested on the COC. Using Table

1, determine if the amount of sample provided is at least as much as the minimum sample amount required. If not, notify the Project Chemist. The Project Chemist should provide further instructions for handling the sample login.

5.1.7 For inorganics analyses on water samples where preservation at a prescribed pH is required, check for the appropriate pH. Refer to Table 2 for those analyses requiring the pH check at the time of receipt. For example, water samples for metals analysis require a pH of <2 and water samples for cyanide analysis require a pH of >12. The pH check is documented on the cooler receipt form which, when completed, is kept with the SDG file. The pH is checked on bottles requiring certain organics analyses, including oil and grease, hydrocarbon, or VOA analyses by the lab department. All pH measurements made by SMO personnel must be performed by pouring a small aliquot of sample from the bottle into a plastic weigh boat. Narrow-range (increments of 0.2 units or less) pH test strips are used. The pH test strips are dipped into the liquid in the weigh boat in order to measure the pH of the sample. Under no circumstances is a pH test strip to be dipped directly into a sample container, due to the possibility of contamination. If further preservation of the sample is needed, the appropriate acid or base is added (up to a maximum of 2mL per liter). The lot number for the preservative added is recorded on the cooler receipt and preservation form as well as the time preserved.

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Note: If acid is added to a metals sample at the time of login, a comment is added to the Service Request indicating to the analyst that the sample was preserved at login. This indicates to the analyst that the 16-hour minimum sample holding requirement listed in the laboratory SOPs applies.

5.1.8 For semivolatile organics analyses on water samples where preservation is necessary for samples with residual chlorine present, check for the presence of residual chlorine (see Table 2 for analyses required). Using a potassium iodide starch test strip, pour a small amount of sample into a weigh boat and dip the strip into the weigh boat. If positive, the test strip will turn purple. Test one bottle per sample and record the result. If the test for residual chlorine is positive, the sample is taken to the laboratory for addition of sodium thiosulfate solution (1mL of 10% to each applicable bottle) and documented. The lot number for the preservative added is recorded on the cooler receipt and preservation form.

5.1.9 Discrepancies and Broken Samples

5.1.9.1 Any discrepancies or concerns from sections 5.1.1 through 5.1.6 above are noted on the COC and/or Cooler Receipt Form and communicated to the Project Chemist. Any resolutions are recorded on the Chain of Custody form, a nonconformity form, or a phone log that is placed in the

service request master file. If a Chain of Custody is not received, information is noted on a CAS Log-In Information sheet (see Appendix).

5.1.9.2When sample identifications on bottles are different than what is on the Chain of Custody, the difference is noted on the Cooler Receipt Form (CRF) and the project chemist is informed, via the "Please Check" Post-it, to check the ID. Once it is logged in on the service request the way the client wants and discrepancies are noted on CRF, a red check is placed on the sample bottle. This informs the lab that the discrepancy has been noted. If there is a discrepancy between the service request identification and the sample bottle identification and no red check is on the sample bottle, the analysts must inform SMO immediately to verify they have the right sample and it can be documented as stated above.

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5.1.9.3 Cleanup procedures are as follows:

Liquids: Broken glass is handled carefully using disposable gloves and disposed of in the Glass Disposal Box. The liquid, including ice, is collected and disposed of as RCRA waste. Any absorbent packing material containing the liquid is collected and disposed of in the RCRA solids waste container.

Soils: Broken glass is handled carefully using disposable gloves and disposed of in the Glass Disposal Box. The solids are collected and disposed of in the RCRA solids waste container along with any packing material contaminated with the sample.

5.1.9.4For VOA samples in VOA vials, EPA Method 5030B states that the size of any bubble caused by degassing upon cooling should not exceed 5-6mm. The presence of air bubble(s) is noted on the CRF if the bubble is $\geq$ 5mm (approximately the size of a small pea). If a bubble this size is present, the cap and septum should be inspected for breakage or leakage. The Project Chemist will be notified if no other vials for the sample can be used (all vials have bubbles).

5.1.10 For EPA CLP work, the following additional steps must be taken:

5.1.10.1Designated Sample Custodian

The SMO department must designate a primary sample custodian who is responsible for the log-in of EPA CLP samples. An alternate representative should also be designated; the EPA PC should be aware of the identity of these people and should be notified if there is a desire to transfer this authority to a different individual.

5.1.10.2Sample Log-In Sheet (DC-1)

This form is used to document receipt and inspection of samples and containers. A DC-1 form (see Appendix) is required for each cooler. It must be completed as the cooler is opened and samples are examined, as described in the applicable CLP SOW. In addition to examining the items found in section 5 of this SOP, the following additional items must be reviewed and/or noted on form DC-1:

- The presence/absence and condition of custody seals.
- The presence/absence of chain-of-custody forms, airbills or airbill stickers, traffic reports or packing lists, and sample tags.
- Custody seal numbers when present
- Airbill or airbill sticker numbers
- Sample tags listed/not listed on the COC records
- Date and Time of receipt
- EPA sample numbers
- Sample tag numbers

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When the DC-1 form is completed, the sample custodian or designated alternate must provide a full signature sign-off on the report; initials are not acceptable.

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5.1.10.3pH Verification - Check the pH as described in section 5.1.6. Any discrepancy from this must be reported to EPA SMO.

5.1.10.4Sample Traffic Reports

A traffic report is required for each Sample Delivery Group. Traffic reports and an SDG cover sheet must be sent to SMO within three days of receipt of the last sample in SDG, as described in the applicable CLP SOW.

5.1.10.5SDG Naming

For EPA CLP work, the following rules must be followed in forming Sample Delivery Groups (SDG). An SDG is defined by the following, whichever is more frequent:

- Each case of field samples, or
- Each 20 field samples in a case, or
- Each 14 calendar day period during which field samples in a case are received. The 14-day period begins with the receipt of the first sample.

The SDG number is the 6-digit EPA sample number of the first sample received in an SDG. When several samples are received at the same time, the lowest alpha, numeric number is used. CAS assigns a unique lab code to each sample. The lab codes are recorded on the Chain of Custody where it is applicable.

5.1.11 Samples received after normal business hours (8-5 Monday – Friday and 8-12 on Saturday) are stored in a cooler in an appropriate refrigerator and are fully processed the following day. Upon receipt, an After Hours Receipt Form is completed and the temperature of the cooler is recorded in accordance with section 5.4 of this SOP (Note: the temperature must be recorded from the temperature blank if one is present). If samples are received the same day they are collected they can be placed in appropriate cold storage without determining cooler temperatures (In this case, samples are considered acceptable if there is evidence that the chilling process has begun and they do not need to meet the criteria of being within 2° C of the required temperature). The location of storage is noted on the After Hours Receipt Form (i.e. Samson, Herk, etc.).

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5.1.12 The chain of custody form will be signed when the log-in procedure is completed (on the next working day if the samples are received after hours).

5.1.13 Courier Service

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CAS provides a Courier Service for our Clients from our Kelso Laboratory Southbound to the Portland Metropolitan area to pick up samples. When picking up samples from Clients, a Courier/After-Hours Sample Receipt Record is filled out and signed by our Courier and also by the Client/Sampler. Information such as date & time of pick-up, the Company name, number of containers, project number and if custody seals were present or added are noted on this Receipt Form. The Courier retains a copy of the Courier/After-Hours Sample Receipt Record and this copy is placed in the Master File once the job is logged into the LIMS system in the laboratory. The original copy is given to the Client at the time the CAS Courier takes possession of the samples.

5.2 Sample Login

5.2.1 Each job received at the laboratory is logged into the Laboratory Information Management System (LIMS). Access to LIMS Login is limited to Sample Management Staff and Project Chemists. The LIMS will assign the next available Service Request number. The Service Request number is made up to identify the CAS lab, the year and then a numeric number (i.e. K0502250: K for the Kelso lab, 05 for the year and then 02250 would be the next number available in the system).

5.2.2 The client and project are identified in the LIMS based on the COC information. The Sample Delivery Group (SDG) sample template is chosen and transferred to the login. If needed, the requested tests are added. The sample identifications, date and time of collection, and date received are entered. The date on which the laboratory takes possession of the samples is defined as the date the COC is signed. For after-hours sample receipt where the after hours receipt form is used, the COC is not signed until the next business day (see 5.1.11). If the collection time is not provided, a conservative estimate of the time is made. In cases where the client and project information is not in LIMS, the PC is contacted to setup the project or give instruction to the SMO staff as to how to set up the project.

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5.2.3 Each test is automatically assigned a container ID in LIMS. The specific containers received are reconciled at the time of login.

5.2.4 The service request report is printed and a master Service Request File is created. Another person in the Sample Management group performs a login review. The master SR file is then given to the Project Chemist for final review before being issued to the laboratories. The Project Chemist reviews the service request form before being issued to the analysts. For analyses with short holding times (generally 48 hours and less), other samples near holding time expiration, and RUSH samples (due within 5 days), a "Temporary Service Request" is issued directly to the applicable department, whose representative signs off on receipt of the service request. SMO also prints a "2-day report" from LIMS that identifies all analyses with holding times expiring within 2 days and due dates within 2 days.

5.2.5 Lab Codes and Sample Identification/Labeling

Each sample is given a unique sample lab code by the LIMS system. This number is designated by the service request number, followed by a dash, a sequential number, a period and a container ID (e.g. K0504567-001.01), where K0504567 represents the service request number, -001 represents the sample and .001 represents the container. Thus, each sample is given a unique ID. Samples are reviewed to make sure the lab codes match the correct sample identification on the service request and that correct bottles were received for the analyses.

5.2.6 Solid Samples Labeling

5.2.6.1 If the quantity of sample given to the laboratory is insufficient for the analyses requested, the sample container should be labeled with Limited Sample Quantity (or something similar) or attach a "LIMITED SAMPLE VOLUME" tag. The project chemist will set the priorities for the analyses and, if possible, estimate the quantity of sample to be used for

each test. This information should be documented and communicated to the lab via a Form V. For example, 8081 use 10 g; metals use 1 g; TCLP use 20 g.

NOTE. Samples that are quantity limited and require multiple analyses from a single container must be identified as soon as possible. Optimally, this should happen during sample login; however, discovery at any time should follow the same process. When it is discovered that a sample is quantity limited, the quantity of wet sample available is estimated and the project chemist is immediately notified. The project chemist should attempt to prioritize the tests most critical to the client (*i.e.*, which test should be performed first) and estimate the sample quantity allotted to each test.

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5.2.6.2 Solid Samples Requiring VOC and Non-VOC Analyses with One Container

When only one container is received and both VOC and non-VOC analyses are requested, SMO will attach a "VOA FIRST" tag to the jar and indicate the tests required.

The VOC department will remove a sample aliquot first for the VOC analyses. The VOC department will handle the sample as if it were a Rush analysis, so that the other non-VOC analyses will not be unduly delayed. The VOC chemist who opens the container will initial and date the "VOA FIRST" tag next to the appropriate test. A ***VOC Analysis First*** note will also be included on the SR.

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Sample aliquots for non-VOC analyses may not be taken from the sample container until the aliquot for the VOC analyses has been removed. Once the aliquot for the VOC analyses has been taken from the sample container, sample aliquots for the non-VOC analyses can be removed as prescribed in the various applicable analytical SOPs.

5.2.6.3 For solid samples requiring VOC and Non-VOC analyses with multiple containers, one of the sample containers will be designated for VOC analyses by either placing a custody seal or a "VOA FIRST" tag on the container.

5.3 Login Review

5.3.1 A peer review of the login and newly generated Service Request (SR) is done by the SMO staff. The SR is compared to the chain-of-custody to ensure that correct and complete information is entered on the SR. Refer to the SMO Login Review sheet (see Appendix).

In some cases (i.e. more complex projects) and at the Project Chemist's discretion, the SMO peer review may be performed by the Project Chemist. In this case, the review of the folder is documented by the Project Chemist when updating LIMS and/or initialing the service request.

5.3.2 As mentioned in section 5.2.3 above, the Project Chemist performs a final review of the login. At a minimum, this must include a close examination of the SR and chain-of-custody to verify that the SR generated by SMO accurately reflects the specifications for the project and samples. The Project Chemist may also need to refer to other project-related information, such as project QAPPs, client communication records, etc. If the SR does not accurately specify the work requirements, is incorrect, or is incomplete, the Project Chemist makes the needed changes and the draft SR file returned to SMO for revision. Once the SR is correct, the Project Chemist documents the review by signing the original SR.

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5.4 Thermometer calibration and temperature measurement

5.4.1 The QA department performs thermometer calibration on all thermometers used to monitor sample storage temperature (see SOP ADM-SEMC). Each storage thermometer is given a unique numerical identification tag if one does not already exist, and all records of calibration are kept in the thermometer calibration notebook. The correction factor is recorded on the thermometer label.

5.4.2 Temperature measurement is performed for coolers using calibrated digital thermometers. The thermometer is plunged into the packing material, if possible, or placed as deep into the cooler as is practical and the lid closed. When coolers are packed such that samples are isolated from the main cooler compartment, via plastic bag and/or insulation (foam, vermiculite, etc.), place the thermometer down into the sample area. When multiple samples are in one large bag, place the thermometer in the bag. Do not just place thermometer on top of the bag or insulating material. The equilibration time is a minimum of 10 minutes.

5.4.3 The correction factor is applied to the temperature given by the thermometer after a measurement, and it is the corrected temperature that is recorded on the CRF. As an example, if the correction factor is -0.5, and the thermometer reads 5.9°C, then the corrected temperature is 5.4°C. If a temperature blank is present, the same thermometer is used to read the temperature blank when the cooler is unpacked. After measurement of the temperatures, all of the information is recorded in the appropriate space on the cooler receipt form.

Note: A temperature blank is generally considered more indicative of sample temperature inside the cooler. Where a temperature blank is present, its temperature reading is considered the *primary* temperature of the cooler and the

second reading obtained from the thermometer placed in the cooler is for additional information.

5.5 Sample Storage, Security, and Internal COC

5.5.1 There are a number of refrigerators, freezers, and room temperature storage areas dedicated to specific storage requirements (e.g. Water VOCs, Soil VOCs, etc...) All of the sample storage facilities are located in the secured area. Samples are held in refrigerators until analysis is completed and reported to the client. Refrigeration of all non-tissue samples is maintained at a temperature of 4 ± 2° C unless otherwise specified by the state, project, or client specific protocols. Exception: Soil and sediment sample for designated for mercury analysis by EPA Method 1631 are stored frozen upon receipt. Tissue samples are stored in freezers at -16 to -24° C. Room temperature sample storage is specified in some cases.

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Note: If a new or moved storage unit is to be placed in service, QA must be notified before using it so it can be monitored for acceptable conditions. QA will document and approve the unit for use prior to using for sample storage. Once SMO is notified, QA will begin regular monitoring.

5.5.2 When samples are labeled accordingly with lab codes, they are placed in appropriate refrigerators in a secured area. This area is secured with combination locks which can be accessed by technical laboratory personnel, project managers, administrative support personnel and all senior staff members. Location of samples is recorded on the Service Request form and in internal COC records.

5.5.3 Internal COC procedures for checking samples in and out are described in the SOP SMO-SCOC *Sample Tracking and Laboratory Chain of Custody*. The SMO department has a Sample Custodian who is responsible for retrieving/returning samples from/to storage for analysts. The Sample Custodian checks the samples back into custody/storage. See the SOP SMO-SCOC for specific guidance.

5.5.4 As an alternative to the Sample Custodian sample retrieval system, analysts may retrieve and check samples out/in directly themselves.

NOTE: Regardless of which procedure is used, the analyst is responsible for taking custody of the sample in LIMS, ensuring the internal chain of custody of samples is accurately documented. It is also the responsibility of the analyst to return samples to the storage area when work is completed, and relinquishing custody in LIMS.

5.5.5 When a soil or sediment sample jar is broken during sample storage a determination has to be made whether or not the sample is salvageable (i.e. whether or not the sample has been completely compromised). If there is any question in determining whether a sample is completely compromised contact the PC. If a tissue sample is broken during storage immediately contact the PC for direction.

5.5.5.1 If some or the entire sample is salvageable scan the broken bottle as "broken" in LIMS. Transfer the sample to a new container (if unsure of the transfer process or there are concerns with contamination, contact the PC or appropriate laboratory department supervisor) and assign a new container ID to the sample in LIMS. Label the new container with a barcode label.

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5.5.5.2 If the sample is not salvageable notify the PC and determine if there is additional sample available for analysis. Scan the broken bottle as "broken" in LIMS and dispose of the sample in the appropriate waste stream (if hazards cannot be determined at the time the sample is lost, place it in a ziplock baggie, label it, and place it on pre-disposal shelf for later determination).

5.5.6 Once the Analytical Report has been mailed to the client, the Internal Chain of Custody record from the bar-coding system database is printed and retained in the Service Request File.

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5.6 Sample Disposal

After all analyses have been completed and the Certified Analytical Report (CAR) has been generated and mailed to the client, the associated samples are pulled from refrigeration and stored on shelves located in the secure storeroom area. An assessment is made of the nature of the samples (i.e. hazardous or non-hazardous) and the samples disposed of accordingly. Water samples are held for 31 days and soil samples for 2 months unless contractual obligations supersede these parameters. Fish and invertebrate animal tissue samples are held at -20°C for 90 days after reporting. After the holding period has expired, samples are disposed of using appropriate disposal procedures provided by the health and safety officer and/or committee. This task is performed by qualified SMO personnel.

5.7 Sample Shipping to Outside Labs

5.7.1 The sample is logged in and the specific product code, or "misc. outside", is used for subcontracted analysis. A list of routinely subcontracted analyses is attached.

5.7.2 For CAS Network Labs using LIMS, the samples are shipped with a chain of custody indicating the analyses to be performed.

5.7.3 For other labs, a purchase order (if non CAS lab) and chain of custody is filled out for work going to another subcontract laboratory. TAT, deliverables,etc. are specified. Prior to shipment, SMO personnel perform a review of the COC against samples subcontracted. Samples to be shipped to an outside lab are stored in a refrigerator near SMO.

5.7.4 A shipping form is completed by SMO and given to the shipping department for shipment.

5.7.5 Samples are prepared for shipping by the shipping department by packing in the appropriate packing material, placing blue ice, samples, and the chain of custody in shipping coolers. Custody seals are signed and dated and placed on the front and/or side of the cooler. The cooler is then sealed with packaging tape. A "Sample" label is placed on the cooler.

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5.7.6 Samples that are relinquished to another laboratory that reports all of their data directly to the client and bills the client directly do not need to be logged in.

6. RECORDS

All sample receipt records, including COC forms, CRFs, Service Requests, sample information, etc. is filed in the master service request file.

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7. CHANGES IN SOP SINCE THE LAST REVISION

7.1 Sec 5.1.2 Added statement to check for sort holds time or rush samples.
7.2 Sec 5.1.2 Removed statement - For WDNR, it should be noted if regular ice was present in the cooler.
7.3 Sec 5.1.3 added language to clarify how to handle short HT samples.
7.4 Sec 5.1.4.1 Added language to clarify how to handle short HT samples.
7.5 Sec 5.1.4.2 Added language to clarify how to handle short HT samples.
7.6 Sec 5.1.7 Added requirement to record the time preserved.
7.7 Sec 5.1.9.7 Removed sentence - For method 1631 samples, inspects the sample for the presence of headspace. Document on the CRF if present.
7.8 Sec 5.5.3 Referenced SMO-SCOC SOP
7.9 Sec 5.5.5 Added procedure to follow when container is broken in the lab.
7.10 Sec 5.4.1 Corrected SOP name.

Table 1

Minimum Sample Volume Requirements

Measurement	Matrix	
Inorganics	**Water (ml)**	**Soil (g)**
Color	50	--
Conductance	100	10
Hardness	100	--
pH	50	50
TSS	200	--
TDS	100	--
TS	100	10
TVS	100	10
Settleable Solids	1000	--
Turbidity	100	--
Total Metals	100	10
Metals w/reductive ppt.	1000	--
Dissolved Metals	100	--
Acidity	100	--
Alkalinity	100	--
Bromide	50	10
Chloride	50	10
Cyanide	500	10
Fluoride	50	10
Ammonia as N	50	10
TKN	500	10
Nitrate+Nitrite	100	10
Nitrate	50	10
Nitrite	50	10
Orthophosphorus	100	10
Total Phosphate	100	10
Sulfate	50	10
Sulfide	500	25
Sulfite	500	--
BOD	1000	50
COD	50	25
TOC	50	25
Total Phenols	500	25
MBAS	500	--
AOX/TOX	500	--

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Table 1

Minimum Sample Volume Requirements (continued)

Measurement	Matrix	
Organics	**Water (ml)**	**Soil (g)**
Oil and Grease	1000	25
DRO	500	30
Pesticides (8081A,8141)	1000	30
PCP (8151M)	40	30
PCBs (8082)	1000	30
PAHs (8270C, 8310)	1000	30
Semivolatiles (8270)	1000	30
GRO	2-40ml vials	30
BTEX (8021B)	2-40ml vials	30
Volatiles (8260B)	2-40ml vials	30
Dioxins	1000	30

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Table 2

Sample Preservation Requirements

Inorganics pH Requirements

Analysis	Preservation requirement (pH)
Metals (total) except CrVI and Hg	<2
TOC	<2
COD	<2
Ammonia	<2
TKN	<2
Total Phosphorus	<2
Nitrate/Nitrite	<2
Sulfide	>9
Cyanide	>12
TOX/AOX	<2

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Semivolatile Organics Residual Chlorine Requirements

Analysis	Requirement
Semivolatile Organics (625 and 8270)	None present
Organochlorine Pesticides (608 and 8081)	None present
Herbicides (8151)	None present

Appendix

Cooler Receipt and Preservation Form
Login Information Sheet
DC-1 Form
SMO Login Review Form
Procedure for Salvaging Broken Samples

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K09_____

Initial Login Review ☐ Revision Review ☐

Check the following information before the sample containers are shelved:

	Y	N	Is the CRF completed? (resolutions noted, etc.)
	Y	N	Are all bottles correctly labeled? (Client name vs. Lab code & number)
	Y	N	Is the Matrix consistent with the Chain of Custody (COC) and the bottles?
	Y	N	Are bottles labeled with the correct shelf number?
NA	Y	N	If indicated on the COC, are samples designated for QC specified on the SR?

Reviewed By:_____ Date:_____

Check the following information on the service request against the information on the COC:

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NA	Y	N	Are sample names spelled correctly on the service request (SR)?
NA	Y	N	Is the date collected for each sample correct on the SR?
NA	Y	N	Is the date received correct on the SR? Multiple dates received?
NA	Y	N	Is the project name correct (as listed on the COC)? Discrepancies noted?
NA	Y	N	Is the project number correct (as listed on the COC)? Discrepancies noted?
NA	Y	N	Is the Tier level correct (as listed on the COC)? Discrepancies noted?
NA	Y	N	If listed on the COC, is the PO Number correct on the SR?
NA	Y	N	Are all the samples indicated on the COC logged in?
NA	Y	N	Are all analyses indicated on the COC logged in?
NA	Y	N	For RUSH TAT, does the due date listed on the SR make sense? Is the Rush flag flipped?
NA	Y	N	If any, are the pertinent comments on the COC indicated on the SR? (i.e. metals lists, volume limitations, hazards, etc.)
NA	Y	N	Has a temporary SR been issued for short hold-times and/or 24-48hr rushes?
NA	Y	N	If preservative was added upon receipt, is it indicated on the SR?
NA	Y	N	Does the SR contain appropriate additional product codes such as: EDD-DOD, Sample Prep. Filter codes, TS-Met?
NA	Y	N	Is the two- Day report printed?
NA	Y	N	If needed, is the Sub-Chain printed for outside shipping?
NA	Y	N	Is the COC signed by SMO?

Reviewed By:_____ Date: _____

Columbia Analytical Services, Inc. PC_____
Cooler Receipt and Preservation Form

Client / Project:_____ Service Request *K09*_____

Received:_____ Opened:_____ By:_____

1. Samples were received via? *US Mail* *Fed Ex* *UPS* *DHL* *GH* *GS* *PDX* *Courier* *Hand Delivered*
2. Samples were received in: (circle) *Cooler* *Box* *Envelope* *Other*_____ *NA*
3. Were custody seals on coolers? NA Y N If yes, how many and where?_____
   If present, were custody seals intact? Y N If present, were they signed and dated? Y N
4. Is shipper's air-bill filed? If not, record air-bill number:_____ NA Y N
   _____ _____ _____
5. **Temperature of cooler(s) upon receipt (°C):** _____ _____ _____ _____
   Temperature Blank (°C): _____ _____ _____ _____
   Thermometer ID: _____ _____ _____ _____
6. If applicable, list Chain of Custody Numbers: _____ _____ _____ _____
7. Packing material used. *Inserts* *Baggies* *Bubble Wrap* *Gel Packs* *Wet Ice* *Sleeves* *Other*_____
8. Were custody papers properly filled out (ink, signed, etc.)? NA Y N
9. **Did all bottles arrive in good condition (unbroken)?** *Indicate in the table below.* NA Y N
10. Were all sample labels complete (i.e analysis, preservation, etc.)? NA Y N
11. Did all sample labels and tags agree with custody papers? *Indicate in the table below* NA Y N
12. **Were appropriate bottles/containers and volumes received for the tests indicated?** NA Y N
13. Were the pH-preserved bottles tested* received at the appropriate pH? *Indicate in the table below* NA Y N
14. Were VOA vials received without headspace? *Indicate in the table below.* NA Y N
15. **Are CWA Microbiology samples received with >1/2 the 24hr. hold time remaining from collection?** NA Y N
16. Was C12/Res negative? NA Y N

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Sample ID on Bottle	Sample ID on COC	Sample ID on Bottle	Sample ID on COC

Sample ID	Bottle Count Bottle Type	Out of Temp	Head-space	Broke	pH	Reagent	Volume added	Reagent Lot Number	Initials	Time

*Does not include all pH preserved sample aliquots received. See sample receiving SOP (SMO-GEN).

Additional Notes, Discrepancies, & Resolutions:_____

Columbia Analytical Services Inc.
Cooler Receipt and Preservation Form

Client / Project: _____ Service Request ***K09*** _____

Sample ID on Bottle	Sample ID on COC	Sample ID on Bottle	Sample ID on COC

Sample ID	Bottle Count Bottle Type	Out of Temp	Head-space	Broke	pH	Reagent	Volume added	Reagent Lot Number	Initials	Time

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Additional Notes, Discrepancies & Resolutions: _____

STANDARD OPERATING PROCEDURE

for

METHYL MERCURY IN WATER BY DISTILLATION, AQUEOUS ETHYLATION, PURGE AND TRAP, AND CVAFS

SOP No.: MET-1630W

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Revision: 0

April 12, 2006

Approved by: _____ Supervisor — 4/12/06 Date

_____ QA Manager — 4-13-06 Date

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_____ Laboratory Manager — 4/13/06 Date

COLUMBIA ANALYTICAL SERVICES, INC.
1317 South 13th Avenue
Kelso, Washington 98626

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Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL

NUMBER: _____

Initials: _____ Date: _____

METHYL MERCURY IN WATER BY DISTILLATION, AQUEOUS ETHYLATION, PURGE AND TRAP, AND CVAFS

1. SCOPE AND APPLICATION

1.1. This method is for determination of methyl mercury (CH_3Hg) in filtered and unfiltered water by distillation, aqueous ethylation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). The method is for the determination of CH3Hg in aqueous samples, ranging from sea water to sewage effluent, based on EPA 1630.

1.2. This method is designed for determination of CH_3Hg in the range of 0.02-5 ng/L and may be extended to higher levels by selection of a smaller sample size.

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1.3. Methyl mercury as defined in this method means all methyl mercury forms and species found in the sample such as: CH_3Hg+, CH_3HgCl, CH_3HgOH, and CH_3HgS-R.

1.4. The detection limit and minimum level of quantitation in this method are usually dependent on the level of background elements rather than instrumental limitations. The method detection limit (MDL; 40 CFR 136, Appendix B) for CH_3Hg has been determined to be 0.02 ng/L when no background elements or interferences are present. The minimum level (ML) has been established as 0.06 ng/L

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2. METHOD SUMMARY

2.1. A 100-2000 mL sample is collected directly into specially cleaned, pretested, fluoropolymer or borosilicate bottle(s) using sample handling techniques specially designed for collection of metals at trace levels.

2.2. For dissolved CH_3Hg, samples are filtered through a 0.45-µm capsule filter.

2.3. Fresh water samples are preserved by adding 4-5 mL/L of pretested 11.6 M HCl, while saline samples ([Cl-] > 500 ppm) are preserved with 2 mL/L of 9 M H_2SO_4 solution, to avoid distillation interferences caused by excess chloride.

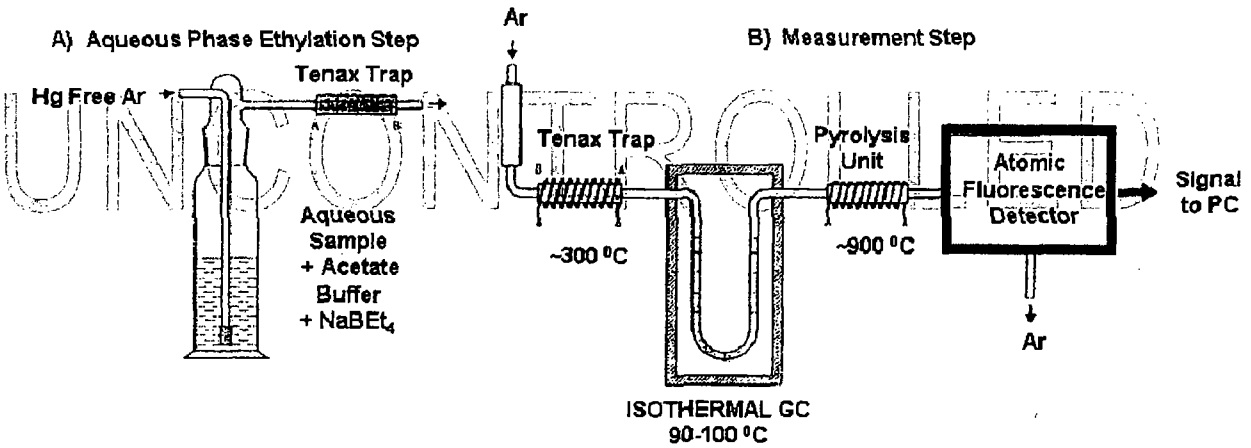
2.4. Prior to analysis, a 45-mL sample aliquot is placed in a specially designed fluoropolymer distillation vessel, and ~ 35 mL of the water is distilled into the receiving vessel at 125°C under Argon flow.

2.5. After distillation, the sample is adjusted to ~ pH 4.9 with an acetate buffer and ethylated in a closed purge vessel by the addition of sodium tetraethyl borate (STEB or $NaBEt_4$).

2.6. The ethyl analog of CH_3Hg, methylethyl mercury (CH_3CH_2 -Hg-CH_3), is separated from solution by purging with Argon onto a Tenax ® trap.

2.7. The trapped methylethyl mercury (MeEtHg) is thermally desorbed from the trap via argon that carries the desorbed organo-mercurials through a GC column, then onto a pyrolytic decomposition column, which converts organo-mercurial forms to elemental mercury (Hg^0), and finally into the cold-vapor atomic fluorescence spectrometer (CVAFS) for detection.

Figure 1: Schematic of Apparatus



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3. DEFINITIONS

3.1. **Dissolved Methyl Mercury** - All distillable CH3Hg forms and species found in the filtrate of an aqueous solution that has been filtered through a 0.45 micron filter.

3.2. **Methyl Mercury** - Mono Methylmercury = MMHg = Methyl Mercury = MeHg = CH_3Hg . All acid-distillable Hg, which, upon reaction with NaBEt4 yields methylethyl mercury. This includes, but is not limited to, CH_3Hg+, strongly organo-complexed CH_3Hg compounds, adsorbed particulate CH_3Hg, and CH_3Hg bound in microorganisms. In freshly collected samples, dimethyl mercury ($(CH_3)_2Hg$) will not be recovered as CH_3Hg, but in samples which have been acidified for several days, most $(CH_3)_2Hg$ has broken down to CH_3Hg. In this method, CH_3Hg and total recoverable CH_3Hg are synonymous.

3.3. **Analysis Sequence** - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample analyses interspersed with various quality control checks. The sequence is ≤ 20 samples and concurrent QC checks.

3.4. **Ethylation Blank** – A minimum of one Ethylation blank is run for each calibration curve. The ethylation blank is run on clean DIH_2O exactly as standards (i.e. with acetate buffer and ethylating reagent and purged onto a trap). The peak height or area of the ethylation blank (or mean of multiple ethylation blanks) is subtracted from the area of each standard to establish the calibration factors.

3.5. **Ethylating Agent** – Sodium Tetra Ethyl Borate or STEB or $NaBEt_4$.

3.6. **Matrix Spike** (MS) - In the matrix spike analysis, a predetermined quantity of standard solution of analyte is added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for analyses. Percent recoveries are calculated for the analyte detected.

3.7. **Matrix Spike Duplicate** (MSD) - In the matrix spike duplicate analysis, a duplicate predetermined quantity of standard solution of analyte is added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike duplicate is to evaluate the effects of the sample matrix on the method used for analyses. Percent recoveries are calculated for the analyte detected. The relative percent difference (RPD), between the matrix spike and matrix spike duplicate is calculated and used to assess analytical precision.

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3.8. **Method Blank** - The method blank is an artificial sample designed to monitor introduction of artifacts into the process. The method blank consists of all reagents, carried through the entire analytical procedure. Either the concentration or peak height of the method blank is subtracted from the concentration or peak height of the samples, before calculating sample concentrations.

3.9. **Quality Control Sample (QCS):** A sample containing CH_3Hg at known concentrations. The QCS is obtained from a source external to the laboratory, or is prepared from a source of standards different from the source of calibration standards. It is used as an independent check of instrument calibration and is not carried through the whole method, but just ethylated as the calibration standards are.

3.10. **Ongoing Precision Recovery (OPR)** - A standard analyzed at the beginning and end of an analytical sequence. The spiked standard is carried through the whole method and is used to verify the ongoing validity of the method.

3.11. **Standard Reference Material (SRM)** - A sample with a certified concentration.

4. INTERFERENCES

4.1. Extreme care must be used in preventing ambient water samples from becoming contaminated during the sampling and analysis process. Samples may become contaminated by numerous routes. Potential sources of trace metal contamination during sampling include: metallic or metal-containing labware (e.g., talc gloves that contain high levels of zinc), containers, sampling equipment, reagents, and reagent water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust. Even human contact can be a source of trace metal contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation.

4.2. Contamination control Philosophy—The best way to control contamination is to completely avoid exposure of samples to contamination in the first place. Avoiding exposure means performing operations in an area free from contamination. Two of the most important factors in avoiding/reducing contamination are (1) an awareness of potential sources of contamination and (2) strict attention to the work being done. It is imperative that the procedures described in this method be carried out by well-trained, experienced personnel.

4.2.1. Use a clean environment—The ideal environment for processing samples is a class 100 clean room. If a clean room is not available, all sample preparation should be performed in a class 100 clean bench or a nonmetal glove box fed by mercury-free and particle-free air or nitrogen. Digestions should be performed in a nonmetal fume hood situated, ideally in the clean room.

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4.2.2. Minimize exposure—The apparatus that will contact samples, blanks, or standard solutions should be opened or exposed only in a clean room, clean bench, or glove box so that exposure to an uncontrolled atmosphere is minimized. When not in use, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean zip-type bags.

4.2.3. Clean work surfaces—Before a given batch of samples is processed, all work surfaces in the hood, clean bench, or glove box in which the samples will be processed should be cleaned by wiping with a lint-free cloth or wipe soaked with reagent water.

4.2.4. Wear gloves—Sampling personnel must wear clean, non talc gloves during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on.

4.2.5. Use metal-free apparatus—All apparatus used for determination of CH_3Hg at ambient water quality criteria levels must be nonmetallic and free of material that may contain metals.

4.2.6. Construction materials—Only fluoropolymer or borosilicate glass containers should be used for samples that will be analyzed for Hg because Hg vapors can diffuse in or out of other materials, resulting in results that are biased low or high. All materials, regardless of construction, that will directly or indirectly contact the sample must be cleaned using the procedures in this method and must be known to be clean and mercury free before proceeding.

4.2.7. Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of apparatus so that contamination can be traced, and logbooks or spreadsheets should be maintained to track the sample from the container through the labware to introduction into the instrument. It may be useful to dedicate separate sets of labware to different sample types; e.g., receiving waters vs. effluents. However, the apparatus used for processing blanks and standards must be mixed with the apparatus used to process samples so that contamination of all labware can be detected.

4.2.8. The laboratory or cleaning facility is responsible for cleaning the apparatus used by the sampling team. If there are any indications that the apparatus is not clean when received by the sampling team (e.g., ripped storage bags), an assessment of the likelihood of contamination must be made.

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4.2.9. Contamination by carryover—Contamination may occur when a sample containing a low concentration of CH_3Hg is processed immediately after a sample containing a relatively high concentration. When an unusually concentrated sample is encountered, an ethylation blank should be analyzed immediately following the sample to check for carryover. Samples known or suspected to contain the lowest concentration of CH_3Hg should be analyzed first followed by samples containing higher levels.

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4.2.10. Contamination by samples—Significant laboratory or instrument contamination may result when untreated effluents, in-process waters, landfill leachates, and other samples containing high concentrations of Hg or CH_3Hg are processed and analyzed. This method is not intended for application to these samples, and samples containing high concentrations of trace metals should not be permitted into the clean room and laboratory dedicated for processing trace metals samples.

4.2.11. Contamination by indirect contact—Apparatus that may not directly come in contact with the samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the apparatus that is directly or indirectly used in the collection, processing, and analysis of samples be thoroughly cleaned.

4.2.12. Contamination by airborne particulate matter—Airborne particles are less obvious substances capable of contaminating samples. Samples may be contaminated by airborne dust, dirt, particles, or vapors from unfiltered air supplies; nearby corroded or rusted pipes, wires, or other fixtures; or metal-containing paint. Whenever possible, sample processing and analysis should occur as far as possible from sources of airborne contamination.

4.3. Interferences

4.3.1. Metals: Iron and Sulfur may cause interferences.

4.3.2. Chloride: Distillation of CH_3Hg from solution requires a carefully controlled level of HCl in solution. Distillation will not be quantitative if too little HCl is added, but too much HCl results in co-distillation of HCl fumes, which interfere with the ethylation procedure. Therefore fresh water samples must be preserved only with between 0.3% and 0.5% (v/v) 11.6 M HCl, and salt water samples with between 0.1% and 0.2% (v/v) 9 M H_2SO_4.

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4.3.3. Nitric Acid: Samples preserved with nitric acid (HNO_3) cannot be analyzed for CH_3Hg as the analyte is partially decomposed in the distillation step by this reagent.

4.3.4. Molecular Interference: The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause "quenching" of the excited atoms. The Tenax® trap eliminates quenching due to trace gases, but it still remains the analysts' responsibility to ensure high purity inert carrier gas and a leak-free analytical train. In some rare cases (such as oil polluted water) low molecular weight organic compounds may purge with the methylethyl mercury and collect on the trap, subsequently resulting in signal quenching during elution. Such cases are best treated by sample dilution prior to distillation.

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4.3.5. Inorganic Mercury and TOC: A positive artifact is possible with the distillation procedure in cases where high inorganic Hg concentrations are present (Reference 7 in Reference 1). In natural waters, approximately 0.01 to 0.05% of the ambient inorganic Hg in solution may be methylated by ambient organic matter during the distillation step. In most waters, where the percent CH_3Hg is 1-30% of the total, this effect is trivial. However, the analyst should be aware that in inorganic Hg contaminated waters, the fraction CH_3Hg can be < 1% of the total, and so flagging of the data (as representing a maximum estimate of CH_3Hg concentration) may be warranted. In samples with high levels of divalent mercury (Hg II), solvent extraction may be preferable to distillation (Reference 7 in Reference 1).

5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat, and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods, and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3. Hydrochloric and Sulfuric Acids and Potassium Hydroxide are used in this method. These acids and bases are extremely corrosive and care must be taken while handling them. A face shield should be used while pouring acids. Safety glasses, lab coat and gloves should be worn while working with the solutions.

5.4. Chronic mercury exposure may cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability, and nervousness. Organo-mercurials may cause permanent brain damage. Because of the toxicological and physical properties of the Hg, pure standards should be handled only by highly trained personnel thoroughly familiar with handling and cautionary procedures and associated risks. **High concentrations of methyl mercury can be fatal!**

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5.5. CAS purchases a dilute standard solution of methyl mercury for this method. If primary solutions are prepared, they must be prepared in a fume hood with the utmost caution.

5.6. Hands should be washed thoroughly after each manipulation and before breaks.

5.7. Ethylating agent ($NaBEt_4$) is toxic, gives off toxic gases (triethylboron), and is spontaneously combustible. To discard unused portions of ethylating agent and empty bottles, place into a large beaker of ~10% 1N HCl in the hood, triethylboron will bubble off to the air where it is eventually oxidized to harmless boric acid. Leave the acid beaker in the hood indefinitely, or boil down to half the original volume to destroy residues before discarding as acid waste.

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6. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

6.1. Before samples are collected, the type of data required, (i.e., dissolved or total), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately before removing an aliquot for processing or direct analysis to ensure the sample has been properly preserved.

NOTE: Do not dip pH paper or pH meter into the sample; remove a small aliquot with a clean pipette and test the aliquot pH.

6.2. Samples are collected into rigorously cleaned fluoropolymer bottles with fluoropolymer or fluoropolymer-lined caps. Borosilicate glass bottles may be used if Hg and Hg species are the only target analytes. It is critical that the bottles have tightly sealing caps to avoid diffusion of atmospheric Hg through the threads. **Polyethylene sample bottles must not be used.**

NOTE: Discrete samplers have been found to contaminate samples with Hg at the ng/L level; therefore, great care should be exercised if this type of sampler is used to collect

samples. It may be necessary for the sampling team to use other means of sample collection if samples are found to be contaminated using the discrete sampler.

6.3. Sample filtration—For dissolved CH3Hg, samples and field blanks are filtered through a 0.45-µm capsule filter (Section 7.2). The Sampling Method describes filtering procedures.

6.4. Preservation—Samples are preserved by adding 4-5 mL/L of concentrated HCL (to allow both CH_3Hg and total Hg determination). Saline samples ([Cl-]>500 ppm) are preserved with 2 mL/L of 9 M H_2SO_4 solution. Acid-preserved samples are stable for at least six months, if kept dark and cool.

6.4.1. Samples may be shipped to the laboratory unpreserved if they are (1) collected in fluoropolymer bottles, (2) filled to the top with no head space, (3) capped tightly, and (4) maintained at 0-4EC from the time of collection until preservation. The samples must be acid-preserved within 48 h of sampling.

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6.4.2. Handling of the samples in the laboratory should be undertaken on a mercury-free clean bench.

6.5. Storage—Sample bottles should be stored in clean (new) polyethylene bags until analysis. To maintain CH_3Hg concentrations without degradation, it is necessary to keep acid-preserved samples dark and cool. If properly preserved, samples can be held up at least six months before analysis.

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7. APPARATUS AND EQUIPMENT

7.1. Cold vapor atomic fluorescence spectrometer (CVAFS): Brooks-Rand (Seattle, WA) Model III CVAFS, or equivalent.

7.2. Filter: 45-µm, 15-mm diameter capsule filter (Gelman Supor 12175, or equivalent)

7.3. Flow meter/needle valve capable of reproducibly keeping carrier gas flow at 30 mL/min.

7.4. Flow meter/needle valve capable of controlling and measuring gas flow rate to the purge vessel at 350 ± 50 mL/min.

7.5. Fluoropolymer fittings: Connections between components and columns are made using 6.4-mm O.D. fluoropolymer tubing and fluoropolymer friction-fit or threaded connectors.

7.6. Tenax® traps for Hg speciation. Silanized, blanked with ends plugged with Teflon. 1/4" O.D. x 10 cm length. (Brooks Rand AF-21-00 or equivalent)

7.7. Isothermal GC Unit: The GC column is ~ 0.3 M long borosilicate glass column tubing with 0.25-in. O.D. and 4-mm I.D. bore. The column is silanized, and packed with preconditioned 60/80 mesh 15% OV-3 on Chromasorb WAW-DMSC, held in place with

silanized glass wool plugs. The column is held in a small temperature-controlled isothermal oven made from a heating mantle. (Supelco Inc. custom product or from Brooks Rand

7.8. Pyrolytic Organo-mercury Breakdown Column: A 20-cm length of 7-mm O.D. by 4.5-mm I.D. quartz tubing with the central 10 cm packed with quartz wool. The column is wrapped with 10 cm of 22-gage Nichrome wire that is electrically heated to about 750-900 ^{0}C (bright orange) with ~56 volts from an autotransformer.

7.9. Gold-coated sand trap or gold wire trap for removing mercury from argon line and for trapping mercury exiting the detector: A tube 10-cm x 6.5-mm O.D. x 4-mm I.D. quartz tubing. The tube is filled with 3.4 cm of gold-coated 45/60 mesh quartz sand with the ends plugged with quartz wool. (Brooks Rand, Ltd., Seattle, WA, Part No. AF-20 or equivalent).

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7.10. Traps are fitted with 6.5-mm i.d. fluoropolymer friction-fit sleeves for making connection to the system. When traps are not in use, fluoropolymer end plugs are inserted in trap ends to eliminate contamination. At least 16 traps are needed for efficient operation.

7.11. Computer (Pentium or better) and Windows Mercury Guru software to record and integrate the signal from the spectrometer.

7.12. Pipettors: All-plastic pneumatic fixed-volume and variable pipettors: 20 uL to 10.0 mL.

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7.13. Analytical balance capable of weighing to the nearest 0.0001 g

7.14. Oven able to maintain temperature of 70 to 100 Celsius.

7.15. 50 mL Teflon Bombs (Savillex or equivalent).

7.16. Ultra high-purity argon (grade 5.0)

7.17. Cold vapor generator (bubbler)—180 mL borosilicate glass with standard taper 24/40 neck, fitted with a sparging stopper having a coarse glass frit that extends to within 0.2 cm of the bubbler bottom (Brooks Rand, Frontier Geosciences, Inc., or equivalent).

8. STANDARDS, REAGENTS AND CONSUMABLE MATERIALS

8.1. Reagent water: Water in which mercury is not detected by 1631 total mercury method. 18-megaohm ultra-pure deionized water from a pre-purified (laboratory DI water) source.

8.2. Argon: Grade 5.0 (ultra high-purity, GC grade) inert gas that has been further purified by the removal of Hg using a gold-coated sand trap.

8.3. Hydrochloric acid—Trace-metal purified reagent HCl containing less than 5 pg/mL Hg. CH_3Hg is not stable in concentrated acid, so the acid does not need to be tested for CH_3Hg.

8.4. Sulfuric acid—Trace-metal purified reagent H_2SO_4 containing less than 5 pg/mL Hg. CH_3Hg is not stable in concentrated acid, so the acid does not need to be tested for CH_3Hg.

8.5. Glacial Acetic Acid: Reagent grade. Blank Pre-tested and verified to be low in mercury.

8.6. Potassium Acetate: Neat, reagent grade. Blank Pre-tested and verified to be low in mercury.

8.7. Potassium Hydroxide: Neat, pellets Semiconductor grade (or shown low in Hg).

8.8. Sodium Tetraethyl Borate: 1-g vials. **Use STREM as supplier.**

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8.9. APDC 1% Solution: Weigh 0.1 – 0.2 g APDC (ammonium pyrrolidine dithiocarbamate) to the nearest mg into a 40 mL amber VOA vial. Add water such that the total weight is now 100 times the starting weight, cap tightly and shake to dissolve. The solution may be purified by extraction with three 10 mL aliquots of methylene chloride.

NOTE: This preparation is small and in amber to protect the APDC which is light reactive. It is strongly recommended that the solution be prepared fresh daily.

8.10. Ethylating Agent (Sodium Tetraethyl Borate 1% Solution, STEB, $NaBEt_4$):

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8.10.1. Rinse approximately 20 seven-milliliter Teflon vials with reagent water and arrange in a vial rack in a class-100 clean hood. (Or use amber HPLC auto-sampler vials.)

8.10.2. Pour 100 mL of reagent water into a 125-mL Teflon bottle and add 2.0 g of KOH pellets. Dissolve mixture and place in freezer until ice crystals just begin to form.

8.10.3. Turn on reagent water. Remove wax and tape seal from a 1.0-g ampoule of sodium tetraethyl borate. Open the ampoule and immediately transfer its contents to the 125-mL Teflon bottle, cap tightly, and give a few quick shakes.

8.10.4. Fill the now empty ampoule and its cap with reagent water and sink into a beaker containing water and HCl (the pure borate powder is pyrophoric and could spontaneously-combust when exposed to air if not stabilized by the addition of water).

8.10.5. Shake the borate solution again then transfer to the vials, leaving ample air space for freezing and capping tightly.

8.10.6. Place all the vials in the freezer standing upright.

8.10.7. If any doubt arises about the quality of the ethylating reagent, make a new batch, as old material often gives good results for reagent water spikes, but not for environmental samples. Do not use STEB solid or 1% solution if they have a yellow color.

8.11. 2M Acetate Buffer: 2 M Acetate Buffer:

8.11.1. Add 100 mL reagent water to a Teflon bottle.

8.11.2. Add 19.6 g of Potassium Acetate.

8.11.3. Add 11.8 mL of Glacial Acetic Acid.

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8.11.4. Ethylate with 0.5 mL STEB (1% solution) and purge overnight with argon to remove trace methyl mercury This solution has an indefinite lifetime when stored in Teflon.

8.12. Argon (Ar): Use Grade 5.0 (ultra high purity grade) argon that has been further purified by the removal of mercury using a gold or iodated carbon trap that is located in line between the gas output and the analyzer gas input.

8.13. Stock methylmercury standard: Stock methylmercury standards (1.0 ug/mL= 1,000 ppm) are obtained from Brooks Rand Seattle. Two standards are purchased. The first is MeHgCl and the second (used for QCS), is from a second source and is MeHgOH. Both standards are sold as 1.00 ug/L in 0.5% HOAc and 0.2% HCL (v/v). These solutions are kept in the refrigerator and are stable until the expiration date. (one year)

8.14. MeHg standard A: Pipette 0.100 mL of the stock solution (1ug/mL = 1,000,000 pg/mL) to 100 mL volumetric flask containing ~ 50 mL DIH_2O, 0.5ml HOAc, and 0.2 ml HCL. QS with DIH_2O. The resulting solution contains 1000 pg/mL MeHg. Keep in a tightly closed Teflon bottle in the refrigerator. This expiration date is the same as the stock standard.

8.15. MeHg standard B: Pipette 10.0 mL of MeHg STD B (1,000 pg/mL) to 100 mL volumetric flask containing ~ 50 mL DIH_2O, 0.5ml HOAc, and 0.2 ml HCL. QS with DIH_2O. The resulting solution contains 100 pg/mL MeHg. Keep in a tightly closed Teflon bottle in the refrigerator. This expiration date is the same as the stock standard.

8.16. MeHg standard C: Pipette 1.0 mL of MeHg STD B (1,000 pg/mL) to 100 mL volumetric flask containing ~ 50 mL DIH_2O, 0.5ml HOAc, and 0.2 ml HCL. QS with DIH_2O. The resulting solution contains 10 pg/mL MeHg. Keep in a tightly closed Teflon bottle in the refrigerator. This expiration date is the same as the stock standard.

9. PREVENTIVE MAINTENANCE

9.1. All maintenance activities are recorded in a maintenance logbook kept for each instrument.

9.2. Broad or asymmetrical peaks indicate a problem with the desorption train, such as low gas flow rate, water vapor on the trap(s), or a GC column damaged by chemicals or overheating. Replace or recondition traps and GC column as needed.

9.3. Traps should be tracked by unique identifiers so that any trap producing poor results can be quickly recognized and discarded. Traps are best when blanked before each use in analysis.

9.4. Bubblers must be kept clean by at least triple rinsing with / storing in DIH_2O between runs. Make sure to fill and drain the dip tube during each rinse. Alternatively store in dilute HCl.

9.5. Occasionally move the Pyrolytic Coil off center (Right and Left) while blanking traps. This is done to remove mercury from the sides of the Pyrolytic tube.

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9.6. Condition the GC column ~ every 2 to 3 months. **SLOWLY** ramp the GC oven up to 180 ^{0}C and condition for 12-16 hours. This purges impurities from the column. See the Model III manual for this procedure.

NOTE: Ramping too quickly causes the oven to overshoot the desired temperature. Going too high (200 ^{0}C) will ruin the column packing material

9.7. Depending on usage the Mercury Source Lamp in the CVASS unit will need to be changed. This procedure is found in the Brooks Rand Manual.

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10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. The acceptance criteria for test performance are listed in Table 1. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the CAS SOP for Documentation of Training, is also the responsibility of the department supervisor/manager.

11. PROCEDURE

11.1. An analytical batch is up to 20 field samples that are prepared with the same reagents and analyzed within the same 12-hour shift. The analytical batch contains the following standards, samples, blanks, and QC Checks:

Method Blank 1
Method Blank 2
Method Blank 3
OPR (Carried through entire method)
Matrix Spike
Matrix Spike Duplicate
Up to 10 samples
QCS (2nd Source ethylated just as a standard)
Matrix Spike
Matrix Spike Duplicate
Up to 10 additional samples
OPR (Carried through entire method)

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For more than 20 samples in a 12 hour shift, the sequence is repeated. Method blanks are analyzed in triplicate. The average of these values is used to correct the sample reading for the contribution of the reagents and the prep tools/containers to the measured methylmercury in unknown samples. The mean blank value should be less than 0.045 ng/L of CH_3Hg, and the variability should be less than 0.015 ng/L of CH3Hg. A mean blank value greater than 0.045 ng/L CH_3Hg or a variability greater than 0.015 ng/L of CH_3Hg is unacceptable for low level ambient analysis.

11.2. Sample Distillation

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11.2.1. Weigh a 45-mL aliquot from a thoroughly shaken, acidified sample, into a 60-mL fluoropolymer distillation vial. Add 200 µL of 1% APDC solution, and replace the distillation cap, such that the tubing extends to the bottom of the vial.

Note: CAS experiments show that light reactive APDC degrades rapidly. It is highly recommended that APDC be made fresh daily and stored in amber bottles.

11.2.2. Repeat this procedure for all samples to be distilled in a set, including three reagent water blanks and spiked samples.

11.2.3. Matrix spikes and matrix spike duplicates—For every 10 or fewer samples, pour two additional 45-mL aliquots from a randomly selected sample. Spike the aliquots at the level specified in Section 12.3 and process them in the same manner as the samples. There should be two MS/MSD pairs for each analytical batch of 20 samples.

11.2.4. For each sample, prepare a 60-mL distillate receiving vial. Add 5.0 mL reagent water to each receiving vial. Cap so that the tubing extends into the water layer.

11.2.5. Record the sample ID associated with each distillation and receiving vial. It is important to develop an unambiguous tracking system, such as the use of engraved vial numbers, because the distillation vials themselves cannot be labeled

11.2.6. Place each prepared distillation vial into one of the holes in the heating block and attach the fluoropolymer tubing to the incoming gas supply from the rotometer manifold. Adjust the gas flow rate through the bubbler to 60 ± 20 mL/min. (40 on the flow meter scale).

11.2.7. As each distillation vial with sample is placed into the heating block, attach the tubing from the receiving vessel to the inlet port of the distillation vessel. Place the corresponding labeled distillation vial into the ice bath adjacent to the heating block.

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NOTE: Be careful that the 5 mL water in the receiver vial does not freeze, blocking the tubing from the distillation vial. This can cause back flow and loss of sample. To prevent this problem:

1) Preheat the heating block to at least 100 °C before adding distillation vessels.
2) Do not completely immerse the receivers in ice block for the first few minutes.
3) Watch the receiver vessels carefully for the first 5 to 10 minute and check that:
   a. the flow meters maintain constant flow at 40 ± 3 on the rotometer.
   b. bubbles are visible in the receiver
   c. warm fumes are distilling over
   d. the receivers are not ice jammed.

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11.2.8. Once all the holes in a heating block are filled, place the aluminum lid over the vessel caps such that all tubing is passing without crimps through the slots, and the lid is making metal-to-metal contact with the block (provides proper heating of the lid).

11.2.9. Turn on the temperature controllers to a pre-set block temperature of 125 ± 3 °C.

11.2.10. Distill the samples until each receiving vial fills to the engraved 40 mL line. This will take ~ 2.5 hr to 4 hr depending on temperatures, gas flow rates, and water.

11.2.11. Different samples and locations on the block will distill at somewhat different rates, so after about 2 hr, all of the tubes should be monitored frequently to avoid over-distillation. As the individual samples fill to the line, they should be removed.

11.2.12. <u>Over-distillation is the greatest potential risk for poor recoveries by this method. If more than the prescribed amount of sample distills over, the risk of HCl fumes co-distilling increases. Chloride and low pH interfere with the ethylation procedure.</u>

11.2.13. If any samples are suspected of over-distillation, they should be checked with pH paper. If the distillate pH is less than 3.5, it should be discarded, rather than analyzed.

11.2.14. Once all of the vials are distilled, the distillates may be stored at room temperature and in the dark for up to 48 h before analysis (loop the fluoropolymer tube around to close off the second port on the receiving vial). Don't refrigerate or store > 48 hr.

11.2.15. The distillation-side (dirty) vials must be scrubbed thoroughly with a test-tube brush and alkaline detergent, then rinsed in reagent water, to remove organics prior to acid cleaning. Then the vials are filled with 10% HCl, recapped with the tubing looped around to close off the port, and placed in an oven at 80°C overnight.

11.3. Ethylation Purge and Trap:

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11.3.1. If standards, ethylation blanks, or QCS are being analyzed, pour 50 mL of reagent water into the bubbler, add 0.3 mL of acetate buffer, the appropriate spike, etc., and 0.05 mL 1% $NaBEt_4$ solution.

11.3.2. Add the ~ 40 mL of distillate to a clean bubbler.

11.3.3. Pipette 0.3 mL of acetate buffer to the bubbler.

11.3.4. Pipette 0.050 mL of freshly thawed 1% $NaBEt_4$ solution. Close the reaction vessel with the bubbler cap, clip the cap on, and swirl gently to mix.

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11.3.5. Allow the contents of the bubbler to react for 17 min. The MMHg in the sample will be converted to volatile methylethyl mercury (MEHg).

11.3.6. After reaction, attach a Tenax ® trap to each bubbler with the 1/4" fluoropolymer fitting, and purge the sample with Argon (~200 mL/min – 40 on the scale) for 17 min.

11.3.7. The trap must be attached such that the gas from the bubbler enters the trap on side A (the crimped and numbered side of the trap).

11.3.8. Once the sample has been purged 17 min, adsorbed water must be dried from the trap. Switch the 4 way valve and purge argon through the trap <u>only</u> for 7 minutes to dry.

11.3.9. After the 7 minute drying, remove the traps and plug the ends with Teflon plugs. The sample is now ready for analysis. Trapped MEHg is quantitatively stable for 6 hours.

11.4. Thermal Desorption, GC-CVAFS analysis:

11.4.1. Ensure the instrument is warmed up with the following conditions:

- Ar flow to GC is on at 10 psi and 30-35 on the flow meter.
- GC oven is at 95 ^{0}C.
- PMT voltage is typically 660 to 700 Volts. Change this in order to achieve an offset as close to 50,000 counts as possible and very steady. (± 15 counts)
- Pyrolytic and Trap Coil controllers are turned on.
- Pyrolytic Coil is centered over glass wool in Pyrolytic Tube.
- A daily Measure Instrument Noise test was done (typically 36-50).

11.4.2. Remove the previous trap from the GC.

11.4.3. Attach next trap to the GC column using a 1/4" fluoropolymer friction fit connector, such that side A (the crimped and numbered side), is facing toward the GC.

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11.4.4. Place the Nichrome wire heating coil around the trap, centered over, and extending beyond the packing material on side A.

11.4.5. Re-connect the argon gas to side B of the trap.

11.4.6. Allow at least 30 sec for the pressure in the system to equilibrate.

11.4.7. Using the mercury Guru software, apply power to the coil around the sample trap for 0.55-0.6 minutes (33-36 seconds using the software's automatic timer), to thermally desorb the ethylated mercury species from the sample trap into the GC column.

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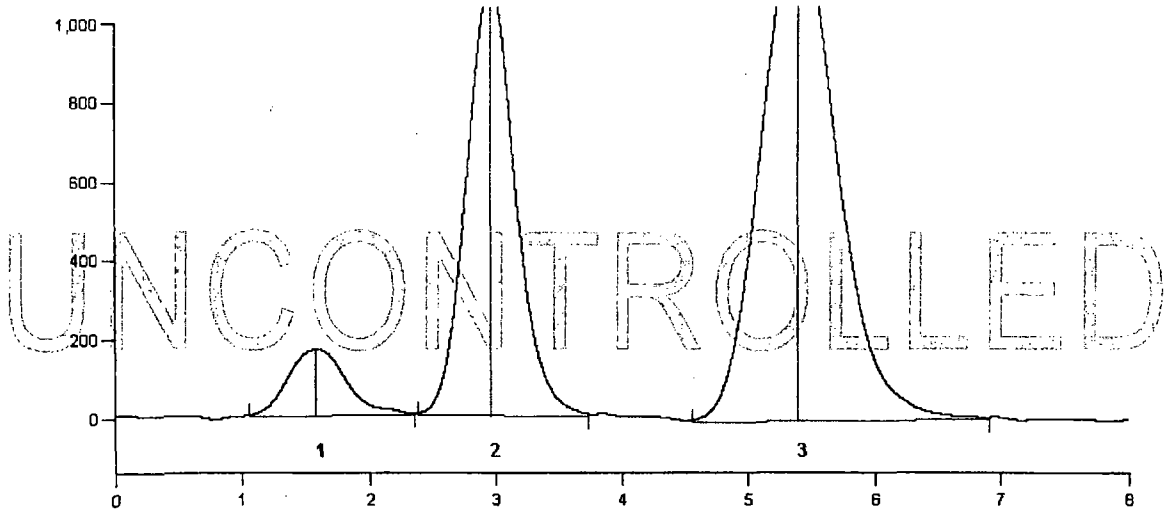
11.4.8. Three peaks should emerge during the run. The first peak (~1.5 min) is Hg ^{o}, which is residual, and non-quantitative. The second peak to emerge (~3 min) is methylethyl mercury (the ethylation product of methylmercury). This is the peak of interest. Following this (~5 min), is the peak for diethyl mercury ($(CH_3CH_2)_2Hg$), which is the ethylation product of Hg (II). If dimethyl mercury ($(CH_3)_2Hg$), were present in the sample, it would appear as a second peak between Hg ^{o} and methylethyl mercury-not fully resolved from the Hg ^{o} See Representative Chromatogram below:

Figure 2: A Representative Chromatogram for ~ 5 pg STD

Peak 1 Hg° Peak 2 MMHg (→MEHg) Peak 3 Hg II (→$HgEt_2$)



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11.4.9. Allow the GC to run ~ 1 min beyond the point that the diethyl mercury (Hg(II)) peak returns to base line. Place the next trap in line and proceed with next sample analysis.

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11.4.10. Peaks generated using this technique should be sharp and close to symmetrical. (Unfortunately, some tailing is typical with this system.) Methylethyl mercury elutes at approximately 2.5 min and has a width at half-height of ~ 20 sec. Earlier peaks
(Hg^{o}, $(CH3)_2Hg$) are sharper, while later peaks (diethyl mercury) are broader.

11.4.11. If only the (Hg^{o}) appears, it usually signifies that either that the pyrolytic column is not on, or that $NaBEt_4$ was not added to the sample, or sample leaked during trapping.

11.4.12. Normally the Hg^{o} peak is small. However, some Hg^{o} is generated by thermal degradation of diethyl mercury during desorption. So, when running samples with a high level of Hg (II), both the Hg^{o} and the diethyl mercury peaks will be bigger.

11.4.13. The ratio of the two peaks is indicative of the quality of the Tenax ® trap. As the trap degrades, the amount of thermal breakdown of organo-mercurials increases. Since the diethyl mercury is much more sensitive to thermal breakdown than the methyl-ethyl mercury, monitoring the latter peak can serve as an early warning for trap replacement. Generally, traps should be replaced any time the Hg^{o} peak grows to be as large as the diethyl mercury peak. (Traps typically last 3 to 6 months.)

11.5. Calibration and standardization

11.5.1. The calibration contains five or more non-zero points and the results of the analysis of at least one bubbler (ethylation) blanks.

11.5.2. Using the procedure in Section 11.3 and 11.4, standards are analyzed by the addition of aliquots of Hg working standards A, B, or C (Section 8.14-8.16) directly into 50 mL of DIH_2O in the bubbler. A typical curve might contain 2, 5, 10, 20, 50, 100 pg for low end analysis, or for higher concentrations: 5, 50, 100, 500, 1000, 2000 pg.

11.5.3. For each calibration point, subtract the mean peak area of the bubbler (ethylation) blank(s) for the batch from the area of each standard. Calculate the calibration factors (CF) for Hg in each of the five to six standards as follows:

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Equation 1

$$CF = (R_S - R_{EB}) / C_S$$

where:

R_S =Peak height or area of the standard
R_{EB} =Peak height or area of the ethylation blank
C_S =Concentration of the standard (ng/L)

Calculate the percent relative standard deviation (%RSD) of the individual calibration factors for all points on the curve.

11.5.4. Calibration criteria are as follows:

(a) There must be a minimum of five non-zero calibration points.
(b) The ethylation blank recovery of the low standard must be 65%-135%
(c) The %RSD for all Calibration Factors is ≤ 15%.

11.5.5. Ongoing precision and recovery: Perform the ongoing precision and recovery test to verify calibration prior to and at the end of each 20 field sample analytical batch.

12. QA/QC REQUIREMENTS

12.1. Initial demonstration of laboratory performance

12.1.1. The analyst shall make an initial demonstration of ability to generate acceptable accuracy and precision. the analyst shall perform the following initial precision and recovery (IPR) study.

12.1.2. Analyze four replicates of the IPR solution (0.5 ng/L) according to the procedure beginning in Section 11.

12.1.3. From the results of the four analyses, compute the average percent recovery (X), and the standard deviation of the percent recovery (s) for CH_3Hg.

12.1.4. Compare s and X with the corresponding limits for initial precision and recovery in Table 2. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the acceptance range, system performance is unacceptable. Correct the problem and repeat the test.

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12.2. In recognition of advances that are occurring in analytical technology, the analyst is permitted certain options to improve results or lower the cost of measurements. These options include automation of the system, solvent extraction in place of distillation, direct electronic data acquisition, or changes in the detector (i.e., CVAAS, AES, ICP/MS). Changes in the principle of the determinative technique, such as the use of colorimetry, are not allowed. If an analytical technique other than the CVAFS technique specified in this method is used, that technique must have a specificity for CH_3Hg equal to or better than the specificity of the technique in this method.

12.2.1. Each time this method is modified, the analyst is required to repeat the procedure in Section 12.1. If the change will affect the detection limit of the method, the lab must demonstrate that the MDL (40 CFR Part 136, Appendix B) is lower than one-third the regulatory compliance level or lower than the MDL of this method, whichever is higher. If the change will affect calibration, the analyst must recalibrate the instrument.

12.2.2. The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

12.2.2.1. The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and the QC officer who witnessed and will verify the analyses and modification.

12.2.2.2. A narrative stating the reason(s) for the modification(s)

12.2.2.3. Results from all quality control (QC) tests comparing the modified method to this method, including the following:

(a) Calibration
(b) Initial precision and recovery
(c) Matrix spike/matrix spike duplicate analysis
(d) Analysis of blanks
(e) Ongoing precision and recovery and quality control sample

12.2.2.4. Data that will allow an independent reviewer to validate each determination by tracking the instrument output to the final result. These data are to include the following:

(a) Sample numbers and other identifiers
(b) Processing dates
(c) Analysis dates
(d) Analysis sequence/run chronology
(e) Sample weight or volume
(f) Copies of logbooks, chart recorder, or other raw data output
(g) Calculations linking raw data to the results reported

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12.3. Method Detection Limits and Method Reporting Limits

12.3.1. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike seven blank matrix (water or soil) samples with MDL spiking solution at a level below the MRL. Follow the analysis procedures in Section 11 to analyze the samples.

12.3.2. Calculate the average concentration found (x) in µg/mL, and the standard deviation of the concentrations (s) in µg/mL for each analyte. Calculate the MDL for each analyte. Refer to the CAS *SOP for The Determination of Method Detection Limits and Limits of Detection*. The MDL study should be done annually.

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12.3.3. The Method Reporting Limits (MRLs) used at CAS are the routinely reported lower limits of quantitation which take into account day-to-day fluctuations in instrument sensitivity as well as other factors. These MRLs are the levels to which CAS routinely reports results in order to minimize false positive or false negative results. The MRL is normally two to ten times the method detection limit.

12.3.4. Laboratory performance is compared to established performance criteria to determine whether the results of analyses meet the performance characteristics of the method.

12.4. Ongoing QC Samples required are described in the CAS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. In general, these include:

12.4.1. The laboratory shall, on an ongoing basis, demonstrate through analysis of the ongoing precision and recovery (OPR) sample and the quality control sample (QCS) that the system is in control.

12.4.2. The determination of CH_3Hg in water is controlled by an analytical batch. An analytical batch is a set of samples distilled with the same batch of reagents, and analyzed during the same 12-hour shift. A batch may be from 1 to as many as 20 samples. Each batch must be accompanied by at least three method blanks, two OPR samples (at start and end of sequence), and a QCS. In addition, there must be one MS / MSD pair for every 10 samples (a frequency of 10%). The lab shall maintain records to define the quality of the data that are generated.

12.4.3. MS / MSD samples are required to demonstrate accuracy and precision and to monitor matrix interferences. Section 12.5 describes the procedure and spike criteria.

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12.4.4. Analyses of blanks are required to demonstrate acceptable levels of contamination. Section 12.6 describes the procedures and criteria for analyzing blanks.

12.5. Method accuracy—To assess the performance of the method on a given sample matrix, the laboratory must perform either matrix spike (MS) and matrix spike duplicate (MSD) sample analyses on 10% of the samples from each site being monitored, or at least one MS/MSD sample analysis for each sample set, whichever is more frequent.

12.5.1. The concentration of the CH_3Hg in the spiked sample shall be determined as follows:

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12.5.1.1.If, as in compliance monitoring, the concentration of CH_3Hg in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1-5 times the background concentration of the sample, whichever is greater.

12.5.1.2. If the concentration of CH_3Hg in a sample is not being checked against a limit, the spike shall be at 1-5 times the background concentration or at 1- 5 times the ML in Table 1, whichever is greater.

12.5.2. Assessing spike recovery

12.5.2.1. Determine the background concentration (B) by analyzing one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 11. If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established a priori.

12.5.2.2. Prepare a spiking solution to produce an appropriate level in the sample.

12.5.2.3. Spike two sample aliquots with the spiking solution and analyze these aliquots as described in Section 11 to determine the concentration after spiking (A).

12.5.2.4. Calculate the percent recovery (P) in each aliquot using Equation 2:

Equation 2

$$P = 100 * (A - B) / T$$

Where:

A=Measured concentration of analyte after spiking
B=Measured concentration of analyte before spiking
P=Percent recovery
T=True concentration of the spike

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12.5.3. Compare the percent recovery (P) with the QC acceptance criteria in Table 2.

12.5.3.1. If P falls outside the range for recovery in Table 2, the CH_3Hg analysis has failed to meet the established performance criteria. If P is unacceptable, analyze the OPR standard. If the OPR is within established performance criteria (Table 2), the analytical system is within specification and the problem can be attributed to interference by the sample matrix.

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12.5.3.2. If the interference can be attributed to sampling, the site or discharge should be re-sampled. If the interference can be attributed to a method deficiency, the analyst must modify the method, repeat the test required in Section 12.1.2, and repeat analysis of the sample and MS/MSD. However, when this method was written, there were no known interferences in the determination of CH_3Hg using this method. If such a result occurs, the lab must thoroughly investigate.

12.5.3.3. If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be outside specified limits. The analyst must identify and correct the problem and reanalyze the sample batch.

12.5.4. Relative percent difference between duplicates—Compute the relative percent difference (RPD) between the MS and MSD results according to Equation 3 using the CH_3Hg concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 12.5.2.4 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

Equation 3

$$RPD = 200 * | D1 - D| / D1 + D2$$

Where:

RPD = Relative percent difference
D1 = Concentration of CH_3Hg in the MS sample
D2 = Concentration of CH_3Hg in the MSD sample

12.5.5. The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 2. If the criterion is not met, the system performance is unacceptable. The problem must immediately be identified and corrected, and the analytical batch reanalyzed.

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12.5.6. As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records maintained. After analyzing five samples in which the recovery passes, compute the average percent recovery (Pa) and the standard deviation of the percent recovery (sp). Express the accuracy assessment as a percent recovery interval from Pa - 2sp to Pa + 2sp. For example, if Pa = 90% and sp = 10% for five analyses, the accuracy interval is expressed as 70-110%. Update the accuracy assessment regularly (e.g., after every five to ten new accuracy measurements).

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12.6. Blanks—Blanks are critical to the reliable determination of CH_3Hg at low levels. The sections below give the minimum requirements for analysis of blanks.

12.6.1. Ethylation blanks—Reagent water typically contains no CH_3Hg. The reagent (ethylation) blank may conveniently be determined by adding 0.3 mL of acetate buffer and 0.050 mL of 1% NaBEt4 solution to 50 mL of reagent water in the reaction vessel. NOTE: Never use a previously ethylated water sample, as a build-up of triethyl boron gas occurs, yielding negative interference and poor chromatography.

12.6.1.1. A single ethylation blank is analyzed with each analytical run, as part of the calibration sequence. This value is used to blank correct the standard curve.

12.6.1.2. The presence of more than 2 pg of CH_3Hg indicates a problem with the reagent water or one of the reagent solutions. An investigation of the cause of the high blank can be made by varying, one at a time, the amounts of buffer, reagent water, and NaBEt4. Because NaBEt4 cannot be purified, a new batch should be made from different reagents and should be tested for Hg levels if the level of CH_3Hg is too high. If the reagent water is found high, this can be remedied by replacing the purification cartridges.

12.6.2. Method blanks

12.6.2.1. The method blanks (distillation blanks) are prepared by the distillation and analysis of 45 mL aliquots of 0.4% HCl acidified reagent water, exactly as if they were samples.

12.6.2.2. Three method blanks should accompany each analytical batch. The mean blank value should be less than 0.045 ng/L of CH_3Hg, and the variability should be less than 0.015 ng/L of CH_3Hg or else the system is unacceptable for low level ambient analysis.

12.6.3. Field blanks

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12.6.3.1. Analyze the field blank(s) shipped with each sample set. Analyze the blank immediately before analyzing the samples in the batch.

12.6.3.2. If CH_3Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 1), or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes.

12.6.3.3. Alternatively, if a sufficient number of field blanks (three minimum) are analyzed to characterize the nature of the field blanks, the average concentration plus 2 STD DEV must be less than the regulatory compliance level or less than 1/2 the level in the associated sample, whichever is greater.

12.6.3.4. If contamination of the field blank(s) and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event.

12.6.4. Equipment blanks—Before any sampling equipment is used at a given site, the laboratory or cleaning facility is required to generate equipment blanks to demonstrate that sampling equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampler check blanks.

12.6.4.1. Bottle blanks—After undergoing the cleaning procedures in this method, bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles should be filled with reagent water acidified to 0.4 - 0.5% HCL and allowed to stand for a minimum of 24 hr. then analyzed for contamination. If any bottle shows signs of contamination, the problem must be identified, the cleaning

procedures corrected or cleaning solutions changed, and all affected bottles cleaned again.

12.6.4.2. Sampler check blanks—Sampler check blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the sampling devices using the same procedures that are used in the field (see Sampling Method). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed.

12.6.4.2.1. Sampler check blanks are generated by filling a large carboy or other container with reagent water and processing the reagent water through the equipment using the same procedures that are used in the field (see Sampling Method). For example, manual grab sampler check blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler check blanks are collected by immersing the submersible pump or intake tubing into the water and pumping water into a sample container.

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12.6.4.2.2. The sampler check blank must be analyzed using the procedures in this method. If CH_3Hg or any potentially interfering substance is detected in the blank, the source of contamination or interference must be identified, and the problem corrected. Equipment must be demonstrated to be free from CH_3Hg and interferences before the equipment may be used in the field.

12.6.4.2.3. Sampler check blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and a subsurface sampling device, a sampler check blank must be run on both pieces of equipment.

12.7. Ongoing precision and recovery (OPR)—To demonstrate that the analysis system is within specified limits and that acceptable precision and accuracy is being maintained within each analytical batch, the analyst shall perform the following operations:

12.7.1. Analyze the OPR solution (0.5 ng/L) prior to the analysis of each analytical batch according to the procedure in Section 11. An OPR must also be analyzed at the end of an analytical run or at the end of each 12-hour shift. Subtract the peak height (or peak area) of the ethlyation blank from the peak height (or area) for the OPR and compute the concentration for the ethylation blank-subtracted OPR.

12.7.2. Compare the OPR with the limits in Table 2. If the concentration is within the spec range, analysis of samples and blanks may proceed. If the concentration is outside

the specified range, the analytical process is not within the specified limits. Correct the problem and repeat the OPR test.

12.7.3. The lab should add results that pass the specification to IPR and previous OPR data and update QC charts to form a graphic representation of lab performance. The laboratory should also develop a statement of laboratory data quality by calculating the average percent recovery (R) and the standard deviation of the percent recovery (sr). Express the accuracy as a recovery interval from R - 2sr to R + 2sr. For example, if R = 95% and sr = 5%, the accuracy is 85- 105%.

12.8. Quality control sample (QCS)—The laboratory must obtain a QCS from a source different from the CH_3Hg used to produce the standards used routinely in this method. The QCS should be analyzed as an independent check of instrument calibration in the middle of the analytical batch (e.g., for a batch of 14 samples, the QCS is analyzed after the 7th sample).

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12.9. Depending on specific program requirements, the laboratory may be required to analyze field duplicates and field spikes collected to assess the precision and accuracy of the sampling, sample transportation, and storage techniques. The relative percent difference (RPD) between field duplicates should be less than 35%. If the RPD of the field duplicates exceeds 35%, the laboratory should communicate this to the sampling team so that the source of error can be identified and corrective measures taken before the next sampling event..

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13. DATA REDUCTION, REVIEW, AND REPORTING

13.1. Calculate the following parameters for each analytical batch:

13.1.1. Ethylation blank (n = 1) or the mean ethylation blank (n > 1)

13.1.2. Ethylation-blank subtracted calibration factor for each standard (Cf_x, Section 11.5.3) and peak measurement for each sample (R_s)

13.1.3. The mean calibration factor (Cf_m), standard deviation of the calibration factor (SD), and relative standard deviation (RSD) of the calibration factor.

13.2. Compute the concentration of CH_3Hg in ng/L (parts-per-trillion; ppt) according to Equation 4:

Equation 4

$$[CH_3Hg](ng/L) = (R_S - R_{EB}) / CF_m * V$$

Where:

R_s = peak height (or area) of signal for CH_3Hg in sample
R_{EB} = peak height (or area) of signal for CH_3Hg in ethylation blank (n = 1) or mean ethylation blank (n > 1)
CF_m = mean calibration factor
V = Sample volume (L)

13.3. The CH_3Hg concentration of the mean method blank is subtracted from the sample concentration calculated above to obtain the **net** in situ CH_3Hg concentration (Equation 5).

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Equation 5

$$[CH_3Hg]_{net} = [CH_3Hg]_{Sample} - [CH_3Hg]_{MB}$$

where:

$[CH3Hg]_{net}$ = net in situ CH_3Hg concentration (ng/L)
$[CH3Hg]_{sample}$ = ethylation-blank corrected concentration of CH_3Hg in the sample (ng/L, Equation 4)
$[CH3Hg]_{MB}$ = concentration of CH_3Hg in the mean method blank (ng/L, Equation 4)

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13.4. Reporting

13.4.1. All results are reported after subtraction of mean method blanks (Equation 5).

13.4.2. Under the conditions described here, the distillation procedure is not 100% efficient in recovering CH_3Hg because not all of the sample volume can be distilled, to avoid co-distillation of HCl. Laboratories should calculate the efficiency of the distillation for their laboratory. This calculation is done by keeping a running mean of the last 30 recoveries calculated for precision and recovery samples (IPR and OPR), excluding all values that are more than two standard deviations from the mean. Since the distillation technique is inherently and reproducibly non-quantitative, all results should be recovery corrected by an empirically derived factor (Equation 6).

Equation 6

$$F = 100 / R$$

where: F = Empirically derived correction factor
R = Recovery (the running mean of the last 30 IPR and OPR samples)

13.4.3. Report all values in ng/L to three significant figures. Report results below the MRL as <0.1 ng/L, or as required by the permitting authority or in the permit.

13.5. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in section 12.

13.6. If any sample result is over the calibration range, prepare and analyze a diluted sample using the appropriate dilution factor to bring within range.

The data packet for the sequence is submitted for review by supervisor or designee.

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13.7. Refer to the SOP for Laboratory Data Review Process for instructions for data review.

14. METHOD PERFORMANCE

14.1. This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

14.2. The method detection limit (MDL) is established using the procedure described in the SOP for *The Determination of Method Detection Limits and Limits of Detection (*ADM-MDL). Method Reporting Limits are established for this method based on MDL studies and as specified in the CAS Quality Assurance Manual.

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15. CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps, are discussed in the applicable section of this (and other applicable) SOP(s). Also, refer to the *SOP for Nonconformity and Corrective Action* for procedures for identifying and documenting such data. Procedures for applying data qualifiers are described in the *SOP for Report Generation* or in project-specific needs.

16. POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents, acids, and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. Environmental threat from solvent and reagent use in this method, can be minimized when recycled or disposed of properly.

17. WASTE MANAGEMENT

17.1. The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

17.2. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the CAS EH&S Manual for details.

18. TRAINING

18.1. Refer to the ***SOP for Documentation of Training*** for standard procedures.

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18.2. Training outline:

18.2.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

18.2.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

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18.2.3. Perform initial precision and recovery (IPR) study as described above . Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file.

18.2.4. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

18.3. Training is documented following the SOP for Documentation of Training.

NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

19. REFERENCES

EPA Method 1630 Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS January 2001

Table 1: Methyl Mercury Analysis Using Method 1630:
Lowest Water Quality Criterion, Method Detection Limit, and Minimum Level

Metal	Lowest Ambient Water Quality Criterion[1]	Method Detection Limit (MDL) and Minimum Level (ML)	
		MDL[2]	ML[3]
Methyl Mercury (CH_3Hg)	none	0.02 ng/L	0.06 ng/L

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NOTES:

1. Lowest of the freshwater, marine, and human health ambient water quality criteria promulgated by EPA for 9 States and the District of Columbia at 40 CFR Part 131on May 4, 1995 (60 FR 22229)

2. Method Detection Limit as determined by the procedure in 40 CFR Part 136, Appendix B.

3. Minimum Level (ML)

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Table 2: Quality Control Acceptance Criteria for Performance Tests In EPA Method 1630

Metal	IPR (Section 9.2)		OPR (Section 9.5)	Method Blanks (Section 9.4)		MS/MSD[1] (Section 9.3)	
	s	X		Max	Mean	%R	RPD
Methyl Mercury (CH_3Hg)	31%	69-131%	67-133%	< 0.1 ng/L	< 0.05 ng/L	65-135%	35%

STANDARD OPERATING PROCEDURE

NITRATE/NITRITE, NITRITE BY FLOW INJECTION ANALYSIS

GEN-353.2
Revision 6
January 5, 2006

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Approved By: _____ Supervisor _____ Date 1/19/06

_____ QA Manager _____ Date 1-19-06

_____ Laboratory Manager _____ Date 1/19/06

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Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL
NUMBER: _____
Initials: _____ Date: _____

NITRATE/NITRITE, NITRITE BY FLOW INJECTION ANALYSIS

1. SCOPE AND APPLICATION

The purpose of this procedure is to determine the concentration of Nitrite, or Nitrate/Nitrite in water and wastewater samples using EPA Method 353.2. This procedure is applicable to determination of Nitrite or Nitrate/Nitrite concentrations greater than 0.02 mg/L in water and wastewater. The Method Reporting Limits (MRLs) and Method Detection Limits (MDLs) are listed in Table 1.

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2. METHOD SUMMARY

2.1. A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite is then determined by diazotization with sulfanilamide, and coupling with N-(1-napthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically. Separate, rather than combined nitrate/nitrite, values are obtained by carrying out the procedure first with, and then without the Cd reduction column, and subtracting NO_2 from NO_3/NO_2 to obtain NO_3.

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2.2. Soil samples may be analyzed following an extraction and filtration procedure.

3. DEFINITIONS

3.1. Analysis Sequence - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration (initial or continuing verification) followed by sample extracts interspersed with calibration standards (CCBs, CCVs, etc...) The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria indicate an out-of-control situation.

3.2. Independent Calibration Verification (ICV) - Initial calibration verification standards which are analyzed after initial calibration with newly prepared standards but prior to sample analysis, in order to verify the validity of the standards used in calibration. The ICV standards are prepared from a materials obtained from a source different from that used to prepare calibration standards.

3.3. Laboratory Control Sample (LCS) - A blank sample fortified with a known amount of target analyte and taken through the entire analysis process. The LCS is used to assess the accuracy of the analysis process.

3.4. Matrix Spike/Duplicate Matrix Spike (MS/DMS) Analysis - In the matrix spike analysis, predetermined quantities of target analytes are added to a sample matrix prior to sample preparation and analysis. The purpose of the matrix spike is to evaluate the effects of the sample matrix on the method used for the analysis. Samples are split into duplicates, spiked, and analyzed as a MS/DMS pair. Percent recoveries are calculated for each of the analytes detected. The relative percent difference (RPD) between the duplicate spikes (or samples) is calculated and used to assess analytical precision.

3.5. Standard Curve - A standard curve is a calibration curve which plots concentrations of a known analyte standard versus the instrument response to the analyte. A calibration is performed using the range for which the intrument response is linear, and uses a linear calibration model. The appropriate criteria for assessing the validity of the calibration curve must be followed prior to quantitation of target analytes in actual sample analyses.

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3.6. Method Blank (MB) - The method blank is an artificial sample composed of analyte-free water or solid matrix and is designed to monitor the introduction of artifacts into the analytical process. The method blank is carried through the entire analytical procedure.

3.7. Continuing Calibration Verification Standard (CCV) - A mid-level standard analyzed at specified intervals. Used to verify that the initial calibration curve is still valid for quantitative purposes.

3.8. Instrument Blank (CCB) - The instrument blank (also called continuing calibration blank) is a volume of clean solvent analyzed on each column and instrument used for sample analysis. The purpose of the instrument blank is to determine the levels of contamination associated with the instrumental analysis itself, particularly with regard to the carry-over of analytes from standards or highly contaminated samples into subsequent sample analyses.

4. INTERFERENCES

4.1. Suspended solids can clog the reduction column and restrict sample flow. Since nitrate/nitrite is found in a dissolved state, the sample may be filtered before analysis.

4.2. Dissolved metals may cause low results. EDTA can be added to the samples to eliminate this interference. Also, 10N NaOH can be added to the samples to precipitate the metals and eliminate this interference.

4.3. The buffer in this method allows analysis of sulfuric acid-preserved samples without pH adjustment. Negative peaks during flow injection analysis, or peaks which split into

groups, are an indication that samples have been excessively acidified, and must be adjusted to a pH between 5.0 and 8.0 with 10 N NaOH or NH_4OH prior to analysis.

4.4. Samples which contain large amounts of oil and grease will coat the surface of the cadmium. The sample may be pre-extracted with an organic solvent to alleviate this interference.

4.5. Highly colored samples may require background correction. To perform a background correction, run the samples through the flow injection analyses without the sulfanilamide reagent. Run buffer through the sulfanilamide line in place of the color reagent.

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5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

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5.3. Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard. Use nitrile or latex gloves while handling pellets or preparing solutions.

5.4. Be cautious of fumes when preparing the NH_4Cl buffer.

5.5. Dispose of culture tubes in the broken glass container.

5.6. Empty waste containers in the hood.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION, AND STORAGE

Samples collected in white plastic bottles are unpreserved. Samples collected in yellow label plastic bottles are preserved. If nitrate and nitrite are to be determined separately, the sample should be stored at 4°C or below, and analyzed within 48 hours. If combined nitrate/nitrite is to be determined, the sample should be preserved with H_2SO_4 to a pH of 2 or less, and stored at 4 ± 2°C for 28 days or less.

7. APPARATUS AND EQUIPMENT

7.1. Lachat QuikChem AE Flow Injection Analyzer and Data System.

7.2. Bran & Luebbe AA3 Flow Injection Analyzer and Data System

7.3. Copper-Cadmium Reduction Column - Lachat Part #50237. For Bran & Luebbe, Irama Part # 165-0301-01.

7.4. Standard Laboratory Glassware and digital pipettors for preparing reagents and dilutions.

7.5. Wrist action shaker

8. STANDARDS, REAGENTS, AND CONSUMABLE MATERIALS

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8.1. 10N NaOH: Add 100 g NaOH to 250 ml DI water very slowly, and swirl to dissolve (reaction is highly exothermic).

8.2. Ammonium Chloride Buffer (Lachcat): Dissolve 85.0 g NH_4Cl and 1.0 g $Na_2EDTA \cdot 2\ H_2O$ in DI water, and dilute to approximately 800 ml. Adjust the pH to 8.5 with 30% NH_4OH, dilute to 1,000 ml with DI water, and mix by inversion.

8.3. Ammonium Chloride Buffer (Bran & Luebbe): Dissolve 97.0 g NH_4Cl and 0.1 g $Na_2EDTA \cdot 2\ H_2O$ in DI water, and dilute to approximately 900 ml. Add 1.0mL stock copper sulfate and mix. Dilute to 1,000 ml with DI water, adjust to a pH of 8.5 with 50% NaOH, and add 2.0mL Brij-35.

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8.4. Sulfanilamide Color Reagent (Lachat): Add 600 ml of DI water and 100 ml phosphoric acid to a 1 l flask. Then add 40.0 g sulfanilamide and 2.0 g N-(1-naphthyl) ethylene diamine dihydrochloride to the flask, and shake to wet. Mix with a magnetic stirrer until all dry chemical is dissolved (approximately 30 minutes), remove the stir bar, and dilute to the mark with DI water. Store the reagent in a labeled brown glass bottle for no more than one month.

8.5. Sulfanilamide Color Reagent (Bran & Luebbe): Add 800 ml of DI water and 185 ml phosphoric acid to a 1 liter flask. Then add 9.1 sulfanilamide and 0.71 g N-(1-naphthyl) ethylene diamine dihydrochloride to the flask, and shake to wet. Mix with a magnetic stirrer until all dry chemical is dissolved (approximately 30 minutes), remove the stir bar, and dilute to the mark with DI water and add 1 mL Brij-35. Store the reagent in a labeled brown glass bottle for no more than one month.

8.6. Copper Sulfate Stock Solution: Dissolve 2.5g copper sulfate in 600mL DIW. Dilute to one liter and mix thoroughly.

8.7. Nitrate Stock Solution: In a 100 mL flask, dissolve 6.068g dried $NaNO_3$ to 100ml final volume with DIW. Concentration = 10,000 ppm. It is standard practice to use the Ion Chromotography Stock.

8.8. Nitrite Stock Solution: In a 250 mL flask, dissolve 12.316 g dried $NaNO_2$ to 250ml final volume with DIW. Concentration = 10,000 ppm. It is standard practice to use the Ion Chromotography Stock

8.9. Working Nitrate Solution: Dilute 1.0 ml of Stock Nitrate Solution to 100 ml with DI water. 1 ml = 100 μg NO_3-N. Prepare fresh weekly.

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8.10. Working Nitrite Solution: Dilute 1.0 ml of Stock Nitrite Solution to 100 ml with DI water. 1 ml = 100 μg NO_2-N. Prepare fresh weekly.

8.11. Calibration Standards: Prepare a series of standards according to one of the options in Table 2. All standards are prepared with DI water, with the exception that standards must be prepared in substitute ocean water (see EPA 353.2) if saline waters are to be analyzed.

8.12. KCl, 2M, dissolve 150g of KCl in 1L deionized water.

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9. PREVENTIVE MAINTENANCE

9.1. No specific maintenance steps are needed other than normal cleaning and inspection of apparatus.

9.2. Change reagent and sampling lines when they are flat.

9.3. For problems encountered with Lachat operation, see Lachat troubleshooting guide.

9.4. For problems encountered with Bran & Luebbe, see Bran & Luebbe troubleshooting guide.

10. RESPONSIBILITIES

10.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

10.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency is also the responsibility of the department supervisor/manager.

11. PROCEDURE

11.1. Sample preparation

11.1.1. Water samples do not require a preparation step. Filtering is included in analysis procedures below.

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11.1.2. For soil sample extraction, perform the following steps.

11.1.2.1. Weigh out 10 g of sample into a 50 mL centrifuge tube.

11.1.2.2. Spike appropriate QC sample with 0.5 mL of 10,000 ppm NO_3 stock solution.

11.1.2.3. Bring to 50mL volume with 2M KCl. The Method blank contains only KCl.

11.1.2.4. Shake samples for 30 minutes on the wrist-action shaker.

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11.1.2.5. Centrifuge samples for 10-20 minutes.

11.1.2.6. Filter supernatant with 0.45μm filter. Samples are now ready for analysis.

11.2. Procedure for Lachat QUIKCHEM AE Analyzer

11.2.1. Turn both the Lachat and computer on. Let warm up for ~ 20 minutes.

11.2.2. Degas carrier and buffer with helium for 5 minutes.

11.2.3. Load method and set up instrument according to Lachat QuikChem AE method.

11.2.4. Fasten reagent lines across the pump and into the reagent bottles. Start pump.

11.2.5. Calibrate with nitrate standards appropriate to the expected NO_3/NO_2 levels in the sample.

11.2.6. Connect cadmium column at the 2nd valve so the sample runs through the column before coloring. For $NO_3 \rightarrow NO_2$ reduction.

11.2.7. For NO_2 determination calibrate with NO_2 standards.

11.2.8. Filter samples through a 0.45 μ syringe type membrane filter into auto sampler vials, and arrange the run according to Table 2. If the initial sample analysis results in a negative peak, due to dissolved metals interference, add 10N NaOH dropwise until the precipate drops out of solution. Centrifuge the sample and analyze.

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11.2.9. Start calibration and sample tray after reagents flow through the flow cell and a steady baseline appears. Refer to Table 3 for a typical run sequence.

11.2.10. CCV (Continuing Calibration Verification) - A CCV must be analyzed following every tenth vial on the autosampler. The CCV is a 3.0 mg/L NO_3-N standard and recovery must be between 2.7 and 3.3 mg/L. The CCV for NO_2-N only is a 3.0 mg/L NO_2 standard.

11.2.11. CCB (Continuing Calibration Blank) - A CCB must be analyzed following every CCV. The CCB is a portion of DI water, and the result must be below the MRL.

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11.2.12. Cleanup - Run 1N HCl through board lines followed by DI water, then NH_4Cl buffer. Remove the cadmium column. Again, pump 1N HCl across the board lines followed by DI water. Pump air through the lines to dry.

11.3. Procedure for Bran & Luebbe Analyzer

11.3.1. Turn on the auto sampler, the pump, the digital colorimeter, then the computer.

11.3.2. Load method and set up instrument according to Bran & Luebbe method.

11.3.3. Fasten correct reagent lines and pump carrier until a stable baseline is achieved. Place lines into appropriate reagents and pump until a stable baseline is achieved.

11.3.4. After a stable baseline is achieved, turn off the pump and switch valve to flow through the cadmium columns (for $NO_3 \rightarrow NO_2$ reduction), turn pump back on and pump until a stable baseline is achieved again.

11.3.5. Calibrate with nitrate standards appropriate to the expected NO_3/NO_2 levels in the sample.

11.3.6. For NO_2 determination calibrate with NO_2 standards.

11.3.7. Filter samples through a 0.45 μ syringe type membrane filter into auto sampler vials, and arrange the run according to Table 3. If the initial sample analysis results in a negative peak, due to dissolved metals interference, add 10N NaOH dropwise until the precipate drops out of solution. Centrifuge the sample, decant supernate, and adjust pH to between 5 and 8 with 5N H_2SO_4, then analyze as normal.

11.3.8. Start calibration and sample tray after reagents flow through the flow cell and a steady baseline appears. Refer to Table 3 for a typical run sequence.

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11.3.9. CCV (Continuing Calibration Verification) - A CCV must be analyzed following every tenth vial on the auto sampler. The CCV is a 2.0 mg/L NO_3-N standard, and recovery must be within 10 percent of expected value. The CCV for NO_2-N only is a 2.0 mg/L NO_2 standard.

11.3.10. CCB (Continuing Calibration Blank) - A CCB must be analyzed following every CCV. The CCB is a portion of DI water, and the result must be below the MRL.

11.3.11. Cleanup - Run 1N HCl through board lines followed by DI water. If the cadmium column valve is open (NO_3/NO_2 analysis), stop the pump, switch valve off, then start the pump again. The cadmium column should be filled with DI water for storage. Remove reagent lines from the DI water and pump the lines dry.

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12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation - The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four LCS aliquots are prepared and analyzed. The average percent recovery must be 90-110% and the RSD < 30%.

12.2. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates at a level near or below the MRL. Follow the procedures starting in Section 11 to analyze the samples. Refer to the CAS SOP for The Determination of Method Detection Limits and Limits of Detection.

12.3. Linear Calibration Range - The Linear Calibration Range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument

response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve falls in the linear range of the instrument. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

12.4. Ongoing QC Samples required are described in the CAS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. In general, these include:

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12.4.1. ICV - A 3.0 mg/L NO_2 for Lachat, and 2.0 mg/L NO_2 for Bran & Luebbe standard is analyzed with every calibration to check the efficiency of the reduction column. Recovery must be within 10% of the true value.

12.4.2. LCS - A Laboratory Control Sample (LCS) must be analyzed with each batch of 20 or fewer samples. Result must be within 90-110% of the true value. Calculate the LCS recovery as follows:

$$\%R = X/TV \times 100$$

Where X = Concentration of the analyte recovered
TV = True value of amount spiked

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12.4.3. Method Blank - A method blank (Deionized Water) must be filtered and analyzed with each batch of 20 or fewer samples. The result must be below the MRL.

12.4.4. Sample Duplicates - One sample per batch of 20 or fewer samples must be analyzed in duplicate. Relative Percent Difference must be $\leq$ 20%.

Calculate Relative Percent Difference (RPD) as:

$$RPD = \frac{|R1 - R2|}{(R1 + R2)/2} \times 100$$

Where R1 = result for the sample
R2 = result for the sample duplicate

12.4.5. Matrix Spikes - One spike sample must be analyzed with each batch of 20 or fewer samples. Recovery must be in the range of 90-110%. Calculate percent recovery (%R) as:

$$\%R = \frac{X - X1}{TV} \times 100$$

Where X = Concentration of the analyte recovered
X1 = Concentration of unspiked analyte
TV = True value of amount spiked

13. DATA REDUCTION, REVIEW, AND REPORTING

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13.1. Calculations

13.1.1. For water samples, the instrument will readout the sample concentration values. No additional calculations are needed other than taking into account any dilutions made.

13.1.2. For soil samples, the instrument will readout the analyzed sample concentration. These are used to calculate the soil sample concentration, taking into account the initial weight, final volume, and any dilutions made.

13.2. Data Reporting

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13.2.1. Report results as follows:

- For Nitrate/Nitrite as "Nitrate/Nitrite as Nitrogen" in mg/L units.
- Report results for Nitrite as "Nitrite as Nitrogen" in mg/L units.
- Report results for Nitrate as "Nitrate as Nitrogen" in mg/L units.
- Soil samples should be reported as method 353.2 Modified in mg/kg (dry wt. basis).

13.2.2. Report results to 3 significant figures unless the sample was diluted. If a dilution was performed, report 2 significant figures.

13.3. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified in section 11 of SOP. Average, RPD, spike level and spike recovery are entered on the analytical spreadsheet for corresponding samples. All data will be initialed, dated and attached to required data quality worksheet.

13.4. The data packet for the sequence is submitted for review by supervisor or designee. The results are transferred to the appropriate report form located in the CAS network

directory R:\WET\WIP. These forms are made from templates located in R:\WET\FORMS.

13.5. Refer to the SOP for *Laboratory Data Review Process* for general instructions for data review.

14. CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s). Also, refer to the SOP for *Nonconformity and Corrective Action* for correct procedures for identifying and documenting such data. Procedures for applying data qualifiers are described in the SOP for *Report Generation* or in project-specific requirements.

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15. METHOD PERFORMANCE

15.1. This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

15.2. The method detection limit (MDL) is established using the procedure described in the SOP for *The Determination of Method Detection Limits* (ADM-MDL). Method Reporting Limits are established for this method based on MDL studies and as specified in the CAS Quality Assurance Manual.

16. POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

17. WASTE MANAGEMENT

17.1. The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

17.2. This method uses a base. Waste base is hazardous to the sewer system and to the environment. All waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be

documented on the treatment by generator record. See the CAS EH&S Manual for details

18. TRAINING OUTLINE

18.1. Review literature (see references section). Review the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

18.2. The next training step is to assist in the procedure under the guidance of an experienced analyst for a period of approximately two weeks. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

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18.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file.

19. REFERENCES

19.1. *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., 1992.

19.2. USEPA, *Methods for Chemical Analyses of Water and Wastes,* EPA-600/4-79-020, March 1983 - Method 353.2.

19.3. Lachat QuikChem Methods.

19.4. Bran & Luebbe Methods.

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TABLE 1

Target Analytes, MRLs, and MDLs (Lachat)

Analyte	Method Detection Limit	Method Reporting Limit
Nitrate/Nitrite-N	0.03 mg/L	0.2 mg/L
Nitrate-N	0.03 mg/L	0.2 mg/L
Nitrite-N	0.02 mg/L	0.2 mg/L

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Target Analytes, MRLs, and MDLs (Bran & Luebbe)

Analyte	Method Detection Limit	Method Reporting Limit
Nitrate/Nitrite-N	0.003 mg/L	0.05 mg/L
Nitrate-N	0.003 mg/L	0.05 mg/L
Nitrite-N	0.002 mg/L	0.05 mg/L

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TABLE 2
Calibration Standards Preparation
Lachat

Routine Calibration Standards

Volume of 100 μg/ml Solution (ml)	Final Volume (ml)	Standard Concentration (mg/L)
0	100	0.00
0.10	100	0.10
0.20	100	0.20
1.00	100	1.00
3.00	100	3.00
5.00	100	5.00
7.00	100	7.00

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Low Level Calibration Standards

Volume of 10 μg/ml Solution (ml)	Final Volume (ml)	Standard Concentration (μg/L)
0	100	0.00
0.2	100	20.0
0.5	100	50.0
0.7	100	70.0
1.0	100	100.0
1.5	100	150.0
2.0	100	200.0

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TABLE 3
Calibration Standards Preparation
Bran & Luebbe

Routine Calibration Standards

Volume of 100 μg/ml Solution (ml)	Final Volume (ml)	Standard Concentration (mg/L)
0.00	100	0.00
0.05	100	0.05
0.50	100	0.50
2.00	100	2.00
4.00	100	4.00

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TABLE 4
Analytical Run Scheme
Lachat

Step	Sample
1	ICB
2	ICV (3.0 mg/L NO_2 Std)
3	CCV-1
4	CCB-1
5	LCS
6	Method Blank
7	Sample
8	Sample Dup
9	Sample Spike
10	Sample
11	Sample
12	Sample
13	Sample
14	Sample
15	CCV-2
16	CCB-2
17-26	10 more Samples
27	CCV-3
28	CCB-3

Repeat steps 5-28 for remainder of samples.

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TABLE 5
Analytical Run Scheme
Bran & Luebbe

Step	Sample
1	ICV (2.0 mg/L NO_2 Std)
2	ICB
3	CCB-1
4	CCV-1
5	LCS
6	Method Blank
7	Sample
8	Sample Dup
9	Sample Spike
10	Sample
11	Sample
12	Sample
13	Sample
14	Sample
15	CCB-2
16	CCV-2
17-26	10 more Samples
27	CCB-3
28	CCV-3

Repeat steps 5-28 for remainder of samples.

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STANDARD OPERATING PROCEDURE

AMMONIA BY FLOW INJECTION ANALYSIS

SOP No.: GEN-350.1

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Revision: 7

May 1, 2007

Approved by: _____ Supervisor _____ Date 5/1/07

_____ QA Manager _____ Date 5-1-07

_____ Laboratory Manager _____ Date 5/1/07

COPY

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Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL
NUMBER: _____
Initials: _____ Date: _____

AMMONIA BY FLOW INJECTION ANALYSIS

1. SCOPE AND APPLICATION

1.1. This procedure is used to determine the concentration of Ammonia in aqueous samples including water, wastewater, and groundwater using EPA Method 350.1 and Standard Methods 4500 NH_3 G. Ammonia in soil samples can be determined following extraction in a potassium chloride solution.

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1.2. This method is applicable for the determination of ammonia concentrations in a range of 0.02 mg/L to 4.0 mg/L. The MRL for this test is 0.05 mg/L and the MDL as been determined at 0.006 mg/L.

2. METHOD SUMMARY

2.1. For EPA 350.1, water samples are distilled into a solution of boric acid or 0.04N sulfuric acid, using the procedure described in and 350.2 and SM 4500 NH_3 B. Standard Methods 4500 NH_3 G may be performed with or without sample distillation.

2.2. Soil and sediment samples are extracted with 2M KCL using a wrist action shaker and extracts analyzed using the water procedure (based on the Plumb extraction procedure).

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2.3. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 660 nm, and is directly proportional to the original ammonia concentration in the sample.

3. DEFINITIONS

3.1. Stock standard solution - a concentrated solution containing a single certified standard that is a method analyte. Stock solutions are used to prepare calibration standards.

3.2. Calibration standards - a solution of analytes prepared in the laboratory from stock standard solutions, diluted as needed, and used to calibrate the instrument response with respect to analytical concentration.

3.3. Laboratory Control Standards (LCS) - a solution of analytes prepared in the laboratory from stock standard solutions purchased or prepared independently from calibration standards.

3.4. Method Blank (MB) - a solution of the laboratory prepared deionized water that is carried through analysis like a sample, to serve as a measure of contamination associated with laboratory storage, preparation, or instrumentation.

3.5. Continuing calibration verification standard (CCV) - a solution of analytes prepared in the laboratory from stock standards to be at approximately the midpoint of calibration curves. CCV's are analyzed every 10 injections to verify that the instrument system performance has not changed during the course of the analytical run.

3.6. Continuing calibration blank (CCB) - a blank solution of deionized water. CCB's are analyzed every 10 injections to verify that the instrument system has not become contaminated during the course of the analytical run.

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3.7. Sample Duplicate - two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. The purpose is to verify the precision associated with the laboratory procedures.

3.8. Matrix Spike - aliquots of sample to which known amounts of an analyte of interest has been added. These are treated exactly the same throughout laboratory analytical procedures. The purpose of a matrix spike is to determine whether the sample matrix contributes bias to the analytical results.

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3.9. Analytical Run Sequence - Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with the instrument calibration or calibration verification followed by samples interspersed with calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

4. INTERFERENCES

4.1. Calcium and magnesium ions may precipitate if present in sufficient concentration. Tartrate or EDTA is added to the sample in-line in order to prevent this problem.

4.2. Color, turbidity and certain organic species may interfere. Turbidity is removed through manual filtration.

4.3. Over-acidic samples create a negative interference resulting in an inverted peak with samples that are at or near the method reporting limit.

4.4. Ensure that the pH of the dilution water and standard NH_3 solution approximates that of the sample.

5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3. Sodium Hydroxide (NaOH) is a strong caustic and a severe health and contact hazard. Use nitrile or latex gloves while handling pellets or preparing solutions.

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5.4. Phenol causes severe burns and is an extreme health hazard through skin absorption. Wear proper protective laboratory clothing including gloves and rinse any exposed skin IMMEDIATELY with copious amounts of water.

6. SAMPLE HANDLING AND PRESERVATION

6.1. Water samples

6.1.1. Samples should be collected in plastic or glass bottles. Bottles must be purchased as pre-cleaned containers or thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis.

6.1.2. Water samples are preserved immediately upon sampling or as soon as possible with H_2SO_4 to pH <2 and stored at 4±2° C until time of analysis. Analysis is to be performed within 28 days of sampling.

6.2. Soils/sediment samples

6.2.1. Samples should be collected in glass jars and stored in a field-moist condition. Ammonia may be lost by volatilization due to drying or thawing.

6.2.2. Extraction is to be performed within 7 days of sampling. Extracts may be preserved with 9N sulfuric acid and stored for up to 28 days until analysis.

7. APPARATUS

7.1. Easy-Still Ammonia Distillation Apparatus. Components are boiling tubes, sloped T-joints, glass stoppers, Allihn condensers, and condenser stems.

7.2. Flow Injection Analyzer with associated software and computer system. The two systems currently in use are listed below.

7.2.1. Lachat QuikChem AE

7.2.2. Bran & Luebbe AutoAnalyzer

7.3. Heating unit associated with the FIA.

7.4. Wrist Action Shaker

7.5. Filter Funnel and Whatman 934-AH or equivalent

7.6. Glassware

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7.6.1. Standard laboratory glassware.

7.6.2. Class A volumetric flasks and pipettes.

8. REAGENTS

8.1. Dechlorinating reagents

8.1.1. Sodium thiosulfate: Dissolve 3.5 g $Na_2S_2O_3C5 \cdot H_2O$ in reagent water and dilute to 1L. One mL of this solution will remove 1 mg/L of residual chlorine in 500 mL of sample.

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8.1.2. Sodium sulfite: Dissolve 0.9 g Na_2SO_3 in reagent water and dilute to 1L. One mL removes 1 mg/L Cl per 500 mL of sample.

8.2. Sodium Hydroxide Solution, 6N, dissolve 48 g of NaOH pellets in 150 ml deionized water. Dilute to 200 ml, cool and store in plastic container.

8.3. KCl, 2M, dissolve 150g of KCl in 1L deionized water.

8.4. Boric Acid Solution, 2% (w/v), dissolve 20.0 g of H3BO3 in deionized water. Dilute to final volume of 1,000 ml.

8.5. Sulfuric acid, 0.04N, 1.1 mL of concentrated sulfuric acid to 1L DI water.

8.6. Sulfuric acid, 9N.

8.7. Lachat analyses:

8.7.1. Sodium Phenolate: Add 83.0g phenol crystals to a 1L volumetric flask containing approximately 500mL of deionized water (DIW). Slowly add 32.0 g NaOH to the

stirring phenolate mixture. Cool, dilute to the mark with DIW, and invert several times to mix. Do not allow solution to stand in hood for excessive amount of time. Refrigerate after use. Do not degas this reagent.

CAUTION: Phenol causes severe burns and is an extreme health hazard through skin absorption. Wear proper protective laboratory clothing including gloves and rinse any exposed skin IMMEDIATELY with copious amounts of water.

8.7.2. Sodium Hypochlorite: Mix 200 mL of Ultra Clorox Bleach (only this brand is recommended) to 250 mL of DIW. Make fresh daily.

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8.7.3. Buffer: In a 1 L volumetric flask dissolve 50.0 g disodium ethylenediamine tetraacetate (Na_2 EDTA) and 5.5 g NaOH in approximately 900mL of DIW. Dilute to the mark and invert several times to mix. Make monthly.

8.7.4. Sodium Nitroprusside (nitroferricyanide): Dissolve 3.50 g sodium nitroprusside in a 1L volumetric containing DIW. Dilute to mark and invert to mix. Do not degas this reagent.

8.7.5. 2M Potassium Chloride (KCl): Dissolve 597 g of potassium chloride in DIW and take to a 4 L final volume.

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8.8. Bran & Luebbe analyses - For analysis performed on the Bran & Luebbe analyzer, refer to the Barn & Luebbe method attachment for reagents used and preparation instructions.

8.9. Stock Standard 10,000 mg/L: In a 1L volumetric flask containing approximately 800 mL of DIW dissolve 38.19 g of ammonium chloride (NH_4Cl) that has been dried for two hours at 110° C. Dilute to the mark and invert to mix.

8.10. Working Standard 100 mg/L: To a 100 mL volumetric flask containing DIW add 1 mL of 10,000 ppm stock standard. Dilute to the mark.

8.11. Calibration standards: See Table 1.

Note: Standards for soil extracts are prepared as in table 1, except that the standards are prepared in 2M KCL INSTEAD of DIW.

8.12. Since the intensity of the color used to quantify the concentration is pH dependent, the acid concentration of the wash water and the standard ammonia solutions should approximate that of the samples.

9. RESPONSIBILITIES

9.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

9.2. It is the responsibility of the department supervisor/manager to document analyst training. Training and proficiency is documented in accordance with the SOP for Documentation of Training (ADM-TRANDOC).

10. PREVENTIVE MAINTENANCE

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10.1. No specific maintenance steps are needed other than normal cleaning and inspection of apparatus.

10.2. Change reagent and sampling lines when they are flat.

10.3. For problems encountered with the analyzer operation, refer to the applicable manufacturer's operating and/or troubleshooting information (Lachat troubleshooting guide, Bran&Luebbe manual).

11. PROCEDURE

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11.1. Sample preparation – water samples

Note: NPDES final effluent samples must be distilled unless otherwise allowed or approved by the client. The distilled results are compared to non-distilled results. If the results are considered equivalent, distillation of subsequent samples of the same effluent is not required. All comparative studies are performed on a client basis and all associated data is kept on file in the General Chemistry lab.

11.1.1. Sample Dechlorination - If the water sample contains residual chlorine, add a dechlorination agent, such as sodium thiosulfate or ascorbic acid, to the sample. Check for residual chlorine by placing a drop of sample on potassium-iodide test paper. Samples should be dechlorinated at the time of collection.

11.1.2. Adjust the pH of a 50-ml sample aliquot to pH 9.5. Add 6 N NaOH dropwise, with mixing, to the sample to adjust the sample pH to 9.5. Check the sample pH with a narrow range pH paper. Add 2.5 ml borate buffer solution; mix sample. Check pH and re-adjust sample to final pH of 9.5 if necessary.

11.1.3. Place the pH adjusted sample in a boiling tube. Add 2-3 micro-porous boiling stones. Assemble the distillation apparatus in the heater block.

11.1.4. Place 5.0 ml of receiving solution in 50-ml centrifuge tube. Place the centrifuge tube in the base slot of the heating block. Select the receiver solution according to analysis method to be used on distillate.

11.1.5. Place the condenser stem in the centrifuge tube, slide cylinder and stem under condenser, and connect stem to condenser with WestClip. When assembled, the condenser tip of the distillation apparatus will be submerged in the receiving solution contained in the centrifuge tube.

11.1.6. Heat the distillation apparatus - Set heater block temperature controls to the following settings:

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RATE1:	15 °C/min	RATE2:	0
TEMP1:	210 °C	TEMP2:	210°C
TIME1:	2.0 Hour (max)	TIME2:	0

Timing Configuration: CONF1

11.1.7. Collect a minimum of 20 ml if distillate.

11.1.8. Discontinue heating. Remove the stopper from the top of the "T"-joint. The stopper removal is needed to prevent the collected distillate from being sucked back into the apparatus during cooling.

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11.1.9. Disconnect the stem from the condenser. Remove the graduated cylinder from the apparatus and dilute the collected distillate to final volume of 50 ml with deionized water.

11.2. Soil sample extraction

11.2.1.1. Weigh out 10 g of sample into a 50 mL centrifuge tube.

11.2.1.2. Spike appropriate QC sample with 0.5 mL of 10,000 ppm NH_3 stock solution.

11.2.1.3. Bring to 50mL volume with 2M KCl. The Method blank contains only KCl.

11.2.1.4. Shake samples for 30 minutes on the wrist-action shaker.

11.2.1.5. Centrifuge samples for 10-20 minutes.

11.2.1.6. Filter supernatant with 0.45μm filter. Samples are now ready for analysis.

11.3. Soil and sediment extraction - Plumb extraction procedure:

11.3.1.1. Weigh 20g of sample into a 50mL centrifuge tube.

11.3.1.2. Spike appropriate QC sample with 1.0 mL of 10,000 ppm NH_3 stock solution.

11.3.1.3. Bring to 50mL volume with 2M KCl. The Method blank contains only KCl.

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11.3.1.4. Shake samples for 30 minutes on the wrist-action shaker.

11.3.1.5. Centrifuge samples for 10-20 minutes.

11.3.1.6. Filter supernatant with 0.45μm filter into a 100mL volumetric flask.

11.3.1.7. Wash the remaining solids with an additional 50mL of 2M KCl and filter into the volumetric flask. Bring to volume with 2M KCl. Samples are now ready for analysis.

11.4. Sample analysis - Lachat system

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11.4.1. Set up instrument according to the Lachat QuikChem method 10-107-06-1-B (See Attachments).

Note: 2M KCl may be used for a sample carrier when running extracts instead of DIW.

11.4.2. The Linear Calibration Range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve falls in the linear range of the instrument. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

11.4.3. Analyze the calibration standards listed in Table 1. The calibration curve is fitted to a linear, least squares model. See Appendix A. The correlation coefficient must be > 0.995. If the calibration criteria are met, continue with the analysis sequence in Table 2. If the LCS recovery is acceptable, proceed with analysis of samples. If not, determine the cause of the problem, correct it, and then recalibrate.

11.4.4. Place samples and QC aliquots in sampler vials and arrange on autosampler according to Table 2.

11.4.5. Repeat sequence bracketing every 10 samples with CCV and CCB. End the sample tray (sequence) with CCV and CCB.

11.5. Sample analysis – Bran&Luebbe system

11.5.1. Set up instrument according to the Bran&Luebbe method US-696D-82X (See Attachments).

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Note: 2M KCl may be used for a sample carrier when running extracts instead of DIW.

11.5.2. The Linear Calibration Range (LCR) must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve falls in the linear range of the instrument. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

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11.5.3. Analyze the calibration standards listed in Table 1 (regular level) or Table 2 (low level). The calibration curve is fitted to a linear, least squares model. See Appendix A. The correlation coefficient must be > 0.995. If the calibration criteria are met, continue with the analysis sequence in Table 2. If the LCS recovery is acceptable, proceed with analysis of samples. If not, determine the cause of the problem, correct it, and then recalibrate.

11.5.4. Ensure that the pH of the dilution water and standard NH_3 solution approximates that of the samples. Place samples and QC aliquots in sampler vials and arrange on autosampler according to Table 3.

11.5.5. Repeat sequence bracketing every 10 samples with CCV and CCB. End the sample tray (sequence) with CCV and CCB.

12. QA/QC REQUIREMENTS

12.1. Initial Precision and Recovery Validation - The accuracy and precision of the procedure must be validated before analysis of samples begins, or whenever significant changes to the procedures have been made. To do this, four LCS aliquots are prepared and analyzed. The average percent recovery must be 85-115% and the RSD< 30%.

12.2. Method Detection Limits - A method detection limit (MDL) study must be undertaken before analysis of samples can begin. To establish detection limits that are precise and accurate, the analyst must perform the following procedure. Spike a minimum of seven blank replicates at a level near or below the MRL. Follow the procedures starting in Section 11 to analyze the samples. Refer to the CAS *SOP for The Determination of Method Detection Limits.*

12.3. CCV (Continuing Calibration Verification): A CCV is analyzed every 10 samples using 2.0 mg/L NH3 standard (from curve). Recovery must fall within 90-110% or 1.8-2.2 mg/L.

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12.4. CCB (Continuing Calibration Blank): A blank consisting of the carrier solution (DIW or KCl). The result must be less than the absolute value of the Method Reporting Limit - |MRL|.

12.5. LCS (Laboratory Control Spike): Analyzed with each batch of 20 or fewer samples. An LCS must be run each day samples are analyzed and have a recovery of 90-110% of true value.

12.6. MB (Method Blank): Deionized water or KCl depending upon samples being analyzed, run every 20 or fewer samples. The result must be less than the absolute value of the Method Reporting Limit - |MRL|.

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12.7. Sample Duplicates: One sample per batch of 20 or less samples must be analyzed in duplicate.

12.8. Matrix Spike: One spiked sample must be analyzed with each batch of 20 or less samples. The spiked sample is usually the same sample used for the duplicate. The recovery criteria is 90-110% for waters and 75-125% for soils.

13. DATA REDUCTION, REVIEW, AND REPORTING

13.1. At the end of the analysis sequence, the calibration data is printed including the calculated standards concentrations, calibration statistics, and slope and intercept of the calibration curve.

13.2. The runtime report printed during the sampling run is turned in with a final report and calibration report.

13.3. For water samples the postrun report is saved to disk and prepared on EXCEL.

13.4. The postrun report for soils is printed at the Lachat, and the numbers transposed to the appropriate benchtsheet. Results are calculated on the bench sheet with dry weights.

13.5. Report results to three significant figures. If sample was diluted report two significant figures.

13.6. Soil/sediment samples and undistilled water samples should be reported as method 350.1 Modified.

14. CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s). Also, refer to the SOP for *Nonconformity and Corrective Action* for correct procedures for identifying and documenting such data. Procedures for applying data qualifiers are described in the SOP for *Report Generation* or in project-specific requirements.

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15. METHOD PERFORMANCE

This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

16. POLLUTION PREVENTION

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It is the laboratory's practice to minimize the amount of solvents, acids and reagent used to perform this method wherever feasible. Standards are prepared in volumes consistent with methodology and only the amount needed for routine laboratory use is kept on site. The threat to the environment from solvent and reagents used in this method can be minimized when recycled or disposed of properly.

17. WASTE MANAGEMENT

17.1. The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

17.2. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the CAS EH&S Manual for details.

17.3. This method uses a base. Waste base is hazardous to the sewer system and to the environment. All waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the CAS EH&S Manual for details

18. REFERENCES

18.1. U.S. Environmental Protection Agency, *Methods for Chemical Analyses of Water and Wastewater*, EPA-600/4-79-020, March 1983 - Method 350.1.

18.2. Methods 4500-NH_3 B,G, *Standard Methods for the Examination of Water and Wastewater*, 20th Ed., 1998.

18.3. Lachat QuikChem Method 10-107-06-1-B.

18.4. Bran & Luebbe Method US-696D-82X.

18.5. *Recommended Protocols for Measuring Selected Environmental Variables in Puget Sound*, January, 1996.

18.6. *Procedures for Handling and Chemical Analysis of Sediment and Water Samples,* Russell S. Plumb, U.S. EPA/Corps of Engineers Technical Committee on Criteria for Dredged Fill Material, May 1981.

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TABLE 1
Calibration Standards Preparation
Regular Level Ammonia

Routine Calibration Standards

Volume of 100 μg/ml Solution (ml)	Final Volume (ml)	Standard Concentration (mg/L)
0	100	0.00
0.05	100	0.10
0.50	100	0.20
2.00	100	1.00
4.00	100	3.00

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TABLE 2
Calibration Standards Preparation
Low Level Ammonia

Low Level Calibration Standards

Volume of 10 μg/ml Solution (ml)	Final Volume (ml)	Standard Concentration (mg/L)
0	100	0.00
0.10	100	0.01
0.50	100	0.05
2.50	100	0.25
5.00	100	0.50

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Note: For low level analysis, change sample tubing from 0.16"ID (orn/yel) to 0.42"ID (orn/orn).

TABLE3
Analytical Run Scheme

Step	Sample
1	CCV-1
2	CCB-1
3	Method Blank
4	LCS
5	Sample
6	Sample Dup
7	Sample Spike
8	Sample
9	Sample
10	Sample
11	Sample
12	Rinse Blank
13	CCV-2
14	CCB-2
15	9 more Samples
16	CCV-3
17-26	CCB-3

Repeat steps 5-28 for remainder of samples.

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APPENDIX A

The calibration is determined using a linear regression that best fits the line of the X:Y pairs. The quality of the fit is determined by calculating the coefficient of determination (R2), also called the correlation coefficient.

The line of regression is calculated as follows:

Start with the equation for a line, y = mx + b. From here the line of regression can be determined.

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$$m = \frac{n\sum(xy) - \sum x \sum y}{n\sum(x^2) - \left(\sum x\right)^2}$$

$$b = \frac{\sum y - m\sum x}{n}$$

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Where:

x = the values of the x variables.
y = the values of the y variables.
n = the number of data points.

Once the line of regression has been determined then the coefficient of determination can be calculated.

$$r^2 = \frac{\left(\sum xy - n\bar{x}\bar{y}\right)^2}{\left(\sum x^2 - \bar{x}\sum x\right) * \left(\sum y^2 - \bar{y}\sum y\right)}$$

ATTACHMENTS

Lachat and Bran & Luebbe Methods

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QuikChem METHOD 10-107-06-1-B

DETERMINATION OF AMMONIA (PHENOLATE) BY FLOW INJECTION ANALYSIS COLORIMETRY

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Written by William R. Prokopy

Applications Group

COPY

Revision date:

24 December 1993

LACHAT INSTRUMENTS

6645 WEST MILL ROAD

MILWAUKEE, WI 53218, USA

QuikChem METHOD 10-107-06-1-B

DETERMINATION OF AMMONIA (PHENOLATE) BY FLOW INJECTION ANALYSIS COLORIMETRY

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LACHAT INSTRUMENTS

6645 WEST MILL ROAD

MILWAUKEE, WI 53218, USA

LACHAT

INSTRUMENTS

QuikChem Method 10-107-06-1-B

Ammonia (Phenolate) in Potable and Surface Waters

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0.01 to 2.0 mg N/L

-- Principle --

This method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonia concentration in the sample.

-- Interferences --

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1. Calcium and magnesium ions may precipitate if present in sufficient concentration. Tartrate or EDTA is added to the sample in-line in order to prevent this problem.
2. Color, turbidity and certain organic species may interfere. Turbidity is removed by manual filtration.

-- Special Apparatus --

1. Heating Unit.

Revised by Karin Wendt/KS and copyrighted © on 24 December 1993 by Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218, USA. Phone: 1-414-358-4200 FAX: 1-414-358-4206. This document is the property of Lachat Instruments. Unauthorized copying of this document is prohibited.

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QUIKCHEM METHOD 10-107-06-1-B

DETERMINATION OF AMMONIA BY FLOW INJECTION ANALYSIS COLORIMETRY

1. SCOPE AND APPLICATION

1.1. This method covers the determination of ammonia in potable and surface waters.

1.2. The method is based on reactions that are specific for ammonia.

1.3. The applicable range is 0.01 to 2.0 mg N/L. The method detection limit is 0.006 mg N/L. Approximately 70 samples per hour can be analyzed.

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2. SUMMARY OF METHOD

2.1. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonia concentration in the sample.

3. DEFINITIONS

3.1. CALIBRATION BLANK (CB) -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.

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3.2. CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3. INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.4. LABORATORY FORTIFIED BLANK (LFB) -- an aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.5. LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background

concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.6. LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.7. LINEAR CALIBRATION RANGE (LCR) -- The concentration range over which the instrument response is linear.

3.8. MATERIAL SAFETY DATA SHEET (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

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3.9. METHOD DETECTION LIMIT (MDL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.10. QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

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3.11. STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4. INTERFERENCES

4.1. Calcium and magnesium ions may precipitate if present in sufficient concentration. Tartrate or EDTA is added to the sample in-line in order to prevent this problem.

4.2. Color, turbidity and certain organic species may interfere. Turbidity is removed by manual filtration.

5. SAFETY

5.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets (MSDS) should be made available to all

personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3. The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1. Phenolate

5.3.2. Nitroferricyanide

6. EQUIPMENT AND SUPPLIES

6.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

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6.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

6.3.1. Autosampler

6.3.2. Multichannel proportioning pump

6.3.3. Reaction unit or manifold

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6.3.4. Colorimetric detector

6.3.5. Data system

6.4. Special apparatus

6.4.1. Heating Unit

7. REAGENTS AND STANDARDS

7.1 PREPARATION OF REAGENTS

Use deionized water (10 megohm) for all solutions.

Degassing with helium:

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140 kPa (20 lb/in^2) through a helium degassing tube (Lachat Part 50100). Bubble He vigorously through the solution for one minute.

Reagent 1. Sodium Phenolate

CAUTION: Wear gloves. Phenol causes severe burns and is rapidly absorbed into the body through the skin.

By Volume: In a **1 L** volumetric flask dissolve **88 mL** of **88% liquified phenol** or **83 g crystalline phenol** (C_6H_5OH) in approximately **600 mL** water. While stirring, slowly add **32 g sodium hydroxide** (NaOH). Cool, dilute to the mark, and invert three times. Do not degas this reagent.

By Weight: To a tared **1 L** container, add **888 g water.** Add **94.2 g** of **88% liquified phenol** or **83 g crystalline phenol** (C_6H_5OH). While stirring, slowly add **32 g sodium hydroxide** (NaOH). Cool and invert three times to mix thoroughly. Do not degas this reagent.

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Reagent 2. Sodium Hypochlorite

By Volume: In a **500 mL** volumetric flask dilute **250 mL Regular Clorox bleach** [5.25% sodium hypochlorite (NaOCl), The Clorox Company, Oakland, CA] to the mark with **water**. Invert to mix.

By Weight: To a tared **500 mL** container add **250 g Regular Clorox bleach** [5.25% sodium hypochlorite (NaOCl), The Clorox Company, Oakland, CA] and **250 g water**. Stir or shake to mix.

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Reagent 3. Buffer

By Volume: In a **1 L** volumetric flask, dissolve **50.0 g disodium ethylenediamine tetraacetate** (Na_2EDTA) and **5.5 g sodium hydroxide** (NaOH) in approximately **900 mL water.** Dilute to the mark and mix with a magnetic stirrer until dissolved.

By Weight: To a **1 L** tared container add **50.0 g disodium ethylenediamine tetraacetate** (Na_2EDTA) and **5.5 g sodium hydroxide** (NaOH). Add **968 g water.** Mix with a magnetic stirrer until dissolved.

Reagent 4. Sodium Nitroprusside

By Volume: To a **1 L** volumetric flask dissolve **3.50 g sodium nitroprusside** (Sodium Nitroferricyanide [$Na_2Fe(CN)_5NO{\cdot}2H_2O$]) dilute to the mark with **water** and invert to mix.

By Weight: To a tared **1 L** container add **3.50 g sodium nitroprusside** (Sodium Nitroferricyanide [$Na_2Fe(CN)_5NO{\cdot}2H_2O$]) and **1000 g water**. Invert to mix.

7.2 PREPARATION OF STANDARDS

Standard 1. Stock Standard 1000 mg N/L

In a 1 L volumetric flask dissolve 3.819 g ammonium chloride (NH_4Cl) that has been dried for two hours at 110°C in about 800 mL water. Dilute to the mark with DI water and invert to mix.

Standard 2. Working Stock Standard Solution 20.0 mg N/L

By Volume: In a 1 L volumetric flask, add 20.0 mL Stock Standard (Standard 1) to the mark with water. Invert to mix.

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By Weight: To a tared 1 L container add about 20 g Stock Standard (Standard 1). Divide the actual weight of the solution added by 0.02 and make up to this resulting total weight with water. Invert to mix.

Set of Eight Working Standards:

2.00	0.80	0.20	0.100	0.040	0.020	0.010	0.00	mg N/L

By Volume: To eight 250 mL volumetric flasks add, respectively,

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25.0	10.0	2.50	1.25	0.50	0.250	0.125	0.0	mL

Standard 2. Dilute each to the mark with water invert to mix.

By Weight: To eight tared 250 mL containers add, respectively, about

25.0	10.0	2.50	1.25	0.50	0.250	0.125	0.0	g

Standard 2. Take the exact weight obtained for each and divide by

0.10	0.04	0.01	0.005	0.002	0.001	0.0005

to get the total weight of the diluted solution. Make up each solution to this total weight with water. Shake before using.

If samples always fall within a narrower range, more standards within this narrower range can be added and standards outside this narrower range can be dropped.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water volume collected should be sufficient to insure a

representative sample, allow for replicate analysis (if required), and minimize waste disposal.

8.2. Ammonia is volatile and will leave the sample slowly, even through polyethylene bottles. The samples should be run within 24 hours. If this cannot be done, they should be frozen. If this cannot be done, the samples should be adjusted to a pH of 3-5 with dilute phosphoric or sulfuric acid. The Federal Register entry which defines standard EPA NPDES and NPDWR methods states that "Manual Distillation is NOT required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies". (see SOURCES). This suggests that the user perform recovery studies on representative sample types, studies which show that the undistilled samples give the same recoveries as the manually distilled samples. Follow EPA Method 350.2 for the complete distillation procedure.

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9. QUALITY CONTROL (USEPA GUIDELINE)

9.1. Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

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9.2. INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1. The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2. Linear Calibration Range (LCR) -- The LCR must be determined initially and verified every 6 months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by +/- 10%, linearity must be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.2.3. Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within +/-10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4. Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

Where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates, t= 2.528 for twenty one replicates]. S = standard deviation of the replicate analyses.

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MDLs should be determined every 6 months, when a new operator begins work, or whenever there is a significant change in the background or instrument response.

9.3 ASSESSING LABORATORY PERFORMANCE

9.3.1. Laboratory Reagent Blank (LRB) – The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

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9.3.2. Laboratory Fortified Blank (LFB) – The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery (Sect. 9.4.2). If the recovery of any analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3. The laboratory must used LFB analyses data to assess laboratory performance against the required control limits of 90-110%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (X) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

$$\text{UPPER CONTROL LIMIT} = \overline{X} + 3S$$

$$\text{LOWER CONTROL LIMIT} = \overline{X} - 3S$$

The optional control limits must be equal to or better than the required control limits of 90-110%. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4. Instruments Performance Check Solution (IPC) -- For all determinations the laboratory must analyze the IPC (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within +/-10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within +/-10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with sample analyses data.

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9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9.4.1. Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of analyte to a minimum of 10% of routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.4.2. Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110%. Percent recovery may be calculate using the following equation:

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$$R = \frac{C_s - C}{s} \text{ X100}$$

Where, R = percent recovery

C_s = fortified sample concentration.

C = sample background concentration.

s = concentration equivalent of analyte added to sample.

9.4.3. If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (sect. 9.3), the recovery problem encountered with the LFM is judged to be either matrix or solution related, not system related.

9.4.4. Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

10. CALIBRATION AND STANDARDIZATION

10.1. Prepare a series of standards, covering the desired range, and a blank by diluting suitable volumes of standard solution (suggested range in section 7.2).

10.4. Calibration the instrument as description in section 11.

10.2. Prepare standard curve by plotting instrument response against concentration values. A calibration curve may be fitted to the calibration solution concentration/response data using the computer. Acceptance or control limits should be established using the difference between the measured value of the calibration solution and the "true value" concentration.

10.3. After the calibration has established, it must be verified by the analysis of a suitable quality control sample (QCS). If measurements exceed +/-10% of the established QCS value, the analysis should be terminated and the instrument recalibrated. The new calibration must be verified before continuing analysis. Periodic reanalysis of the QCS is recommended as a continuing calibration check.

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11. PROCEDURE

11.1. Calibration Procedure

11.2.1. Prepare reagent and standards as described in section 7.

11.2.2. Set up manifold as shown in section 17.1.

11.2.3. Input peak timing and integration window parameters as below:

Sample throughput:		**72 samples/h; 50 s/sample**
Pump speed:		**35**
Cycle period:		**72 s**
Inject to start of peak period:		**22 s**
Inject to end of peak period:		**68 s**
Presentation, Data Window		
Top Scale Response:		**0.50 abs**
Bottom Scale Response:		**0.00 abs**
Segment/Boundaries:	A:	**2.00 mg N/L**
	D:	**0.10 mg N/L**

G: 0.01 mg N/L

H: 0.00 mg N/L

Series 4000/System IV Settings: **Gain = 500 x 1**

11.2.4. Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

11.2.5. Place standards in the autosampler, and fill the sample tray. Input the information required by data system, such as concentration, replicates and QC scheme.

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11.2.6. Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with responses for each standard.

11.3. Analysis Procedure

11.3.1. After a stable baseline has been obtained, start the sampler and perform analysis (please refer to system notes).

11.4. System Notes

11.4.1. Allow 15 min for heating unit to warm up to 60°C.

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11.4.2. If baseline drifts, peaks are too wile, or other problems with precision arise, clean the manifold by the following procedure.

A. Place all reagent lines in deionized water and pump to clear reagents (2 to 5 min).

B. Place all reagent lines in 1 M hydrochloric acid (1 volume concentrated HCl added to 11 volumes of deionized water) and pump for several minutes.

C. Place all reagent lines in deionized water and pump until the HCl is thoroughly washed out.

D. Resume pumping reagents.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Prepare a calibration curve by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve.

12.2. Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed. Any sample whose computed value is less than 5% of its immediate predecessor must be rerun.

12.3. Report results in mg N/L.

13. METHOD PERFORMANCE

13.1. The method performance data are presented as method support data in section 17.2. This data was generated according to Lachat Standard Operating Procedure J001, Lachat FIA Support Data Generation.

14. POLLUTION PREVENTION

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14.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA 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.

14.2. The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

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14.3. For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Society's Department of Government Regulations and Science Policy, 115 16th Street N. W., Washington D. C. 20036, (202) 872-4477.

15. WASTE MANAGEMENT

15.1. The Environmental Protection Agency (USEPA) requires that laboratory waste management practice be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any waster discharge permit and regulations, and by complying with all solid and hazardous waste regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Sect. 14.3.

16. REFERENCES

16.1. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983, Method 350.1

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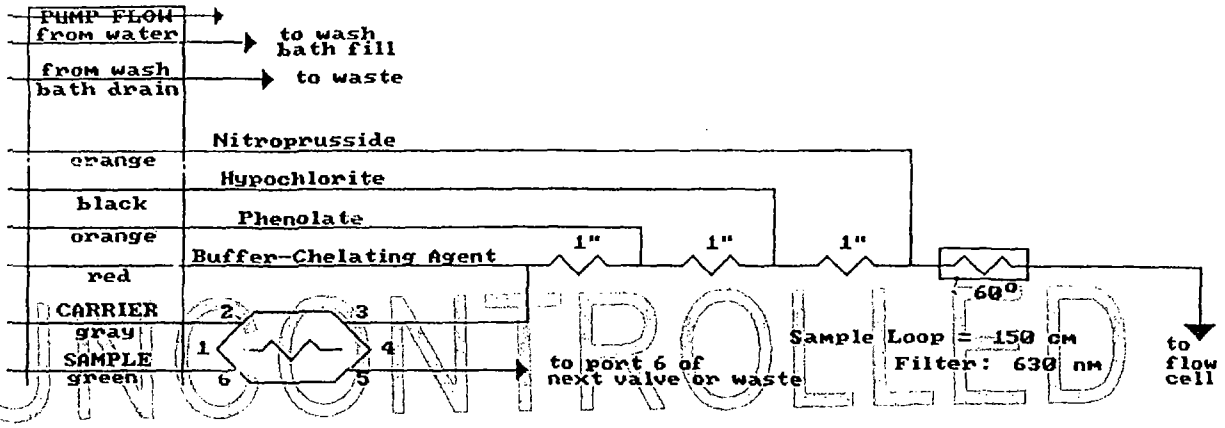
17. TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

17.1. MANIFOLD DIAGRAM:



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CARRIER is Water.

1" is **70.0** cm of tubing on a 1 in coil support

2" is **135** cm of tubing on a 2 in. coil support

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APPARATUS: Standard valve, flow cell, and detector head modules are used. The box shows **650 cm of heated tubing.**

All manifold tubing is **0.8 mm (0.032 in.) i.d.** This is **5.2 uL/cm.**

MANIFOLD DIAGRAM REVISION DATE: 12 August 1993 by N. Liao.

17.2. SUPPORT DATA:

17.2.1. Support Data

QuikChem AE Calibration Report for Calibration 93121001
Method: ammonia 10-107-06-1-B
calibration was first done or last modified on 12/10/93 at 12:13 pm
report prepared on 12/10/93 at 01:18 pm

	Analyte	Units	Average Concentrations Known	Determined	% Residual	Baseline Corrected Average Absorbance
Standard A,	ammonia	mg N/L	2.000	1.991	0.46	0.1157
Standard B,	ammonia	mg N/L	0.800	0.822	-2.77	0.0468
Standard C,	ammonia	mg N/L	0.200	0.207	-3.65	0.0123
Standard D,	ammonia	mg N/L	0.100	0.096	3.71	0.0059
Standard E,	ammonia	mg N/L	0.040	0.040	-0.55	0.0026
Standard F,	ammonia	mg N/L	0.020	0.014	30.81	0.0011
Standard G,	ammonia	mg N/L	0.010	0.010	0.00	0.0006
Standard H,	ammonia	mg N/L	0.000	0.000	+++.++	-0.0000

Calibration Statistics Report

Cal Ref: 93121001
Method: AMMONB

12/10/93 01:21 pm

Channel: ammonia

Correlation Coefficients

Seg	Stds	Full	Chord 1	Chord 2	Chord 3	Chord 4	Chord 5
1	A-G	0.9998	0.9772 ?	0.9998	0.9997	0.9998	0.9994
2	G-H	0.9910	0.7363 ?	0.9787 ?	0.9953	0.9911	0.2604 ?

Percent Standard Deviation in Slope

1	A-G	0.6	6.2	0.5	0.8	0.5	1.0
2	G-H	6.7	42.3	10.4	4.8	6.7	119.2 ?

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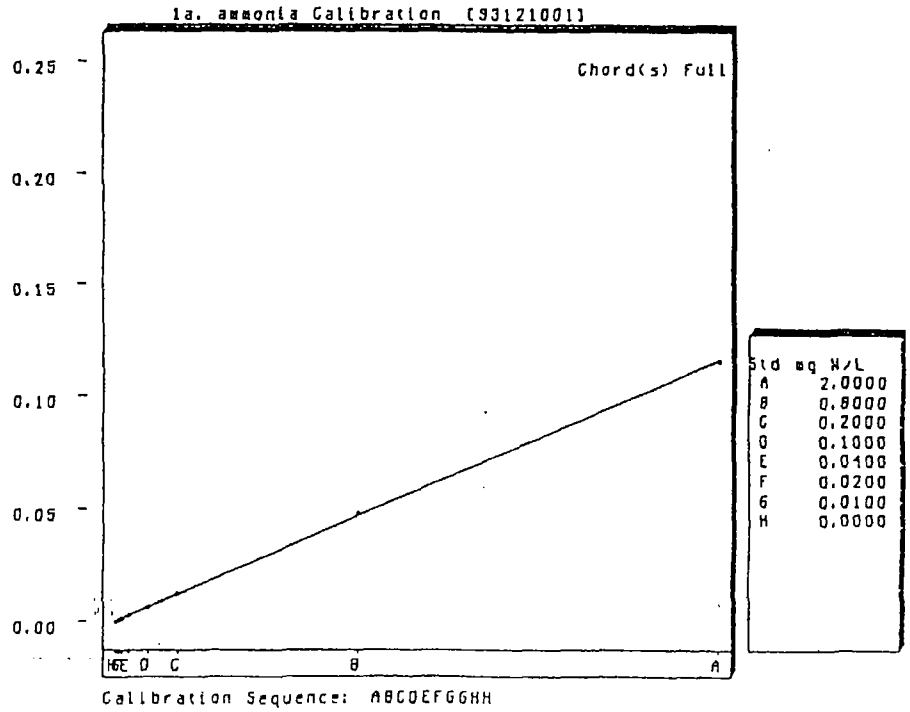
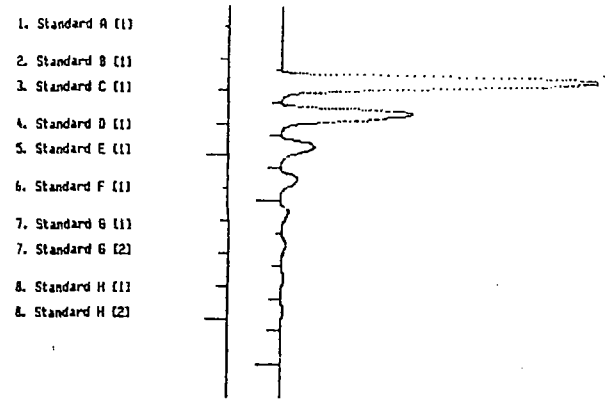
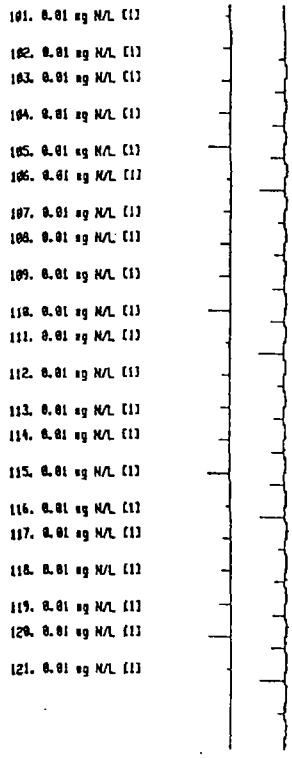


Calibration 12/10/1993, 12:01 pm



UNCONTROLLED

Rack 1 (Ref: 93121001) 12/10/1993, 12:17 pm



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Cup#	Sample ID	ammonia mg N/L
101	0.01 mg N/L	0.010
102	0.01 mg N/L	0.009
103	0.01 mg N/L	0.009
104	0.01 mg N/L	0.009
105	0.01 mg N/L	0.012
106	0.01 mg N/L	0.011
107	0.01 mg N/L	0.012
108	0.01 mg N/L	0.011
109	0.01 mg N/L	0.010
110	0.01 mg N/L	0.010
111	0.01 mg N/L	0.011
112	0.01 mg N/L	0.011
113	0.01 mg N/L	0.010
114	0.01 mg N/L	0.011
115	0.01 mg N/L	0.010
116	0.01 mg N/L	0.008
117	0.01 mg N/L	0.011
118	0.01 mg N/L	0.012
119	0.01 mg N/L	0.013
120	0.01 mg N/L	0.012
121	0.01 mg N/L	0.009

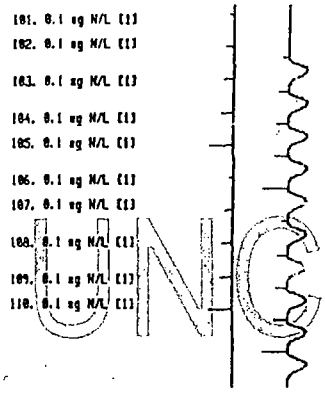
MDL

$\bar{x}$ = 0.011 mg N/L

s = 0.0013

MDL = 0.003 mg N/L

Rack 1 (Ref: 93121002) 12/10/1993, 12:48 pm



Cup#	Sample ID	1 ammonia mg N/L
101	0.1 mg N/L	0.104
102	0.1 mg N/L	0.106
103	0.1 mg N/L	0.109
104	0.1 mg N/L	0.106
105	0.1 mg N/L	0.103
106	0.1 mg N/L	0.102
107	0.1 mg N/L	0.105
108	0.1 mg N/L	0.106
109	0.1 mg N/L	0.107
110	0.1 mg N/L	0.105

Precision

x = 0.105 mg N/L

s = 0.002

RSD = 1.90%

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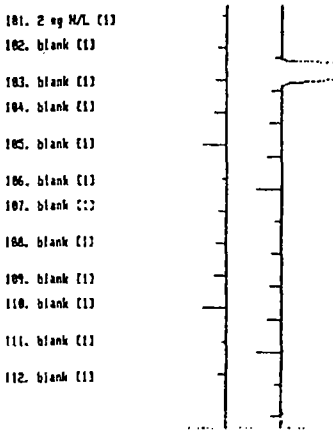
Rack 1 (Ref: 93121003) 12/10/1993, 01:01 pm



Cup#	Sample ID	ammonia mg N/L
101	2 mg N/L	2.072)
102	blank	-0.002(
103	blank	0.000(
104	blank	-0.001(
105	blank	-0.001(
106	blank	0.001(
107	blank	0.000(
108	blank	0.001(
109	blank	-0.000(
110	blank	0.000(
111	blank	-0.003(
112	blank	-0.001(

Carryover

x = -0.0004 mg N/L

s = 0.0012

t = 2.262

-0.0004 +/- 0.0009

EMDL

s = 0.0012

EMDL = 0.006 mg N/L

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AutoAnalyzer Applications

Method No. US- 696D-82X

Ammonia in Water and Wastewater

Range: 0.010-3 mg/l N

Description

The automated procedure for the determination of ammonia utilizes the Berthelot Reaction, in whi the formation of a blue colored compound believed to be closely related to indophenol occurs whe the solution of an ammonium salt is added to sodium phenoxide, followed by the addition of sodiu hypochlorite. A solution of EDTA is added to the sample stream to eliminate the precipitation of th hydroxides of calcium and magnesium.[1,2,3,4,5,6] Sodium nitroprusside is added to intensify the blue color.

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Hardware:
37°C heating bath (MT12)

Pump tubes:
7+1air+1 sampler wash

Performance data using aqueous standards

Test range 0010-3 mg/L N

	AA3	AAII
Sampling rate	40/hr	40/hr
Sample: wash ratio	4:1	4/1
Sensitivity at 3mg/L	0.3576	0.22
Reagent Absorbance	0.062	0.4
Coefficient of Variation	0.429	1.2
30 replicates at 1.5mg/L		
Pooled standard deviation	0.013mg/L	NA
25 at 5 levels		
Correlation coefficient (Linear)	0.9993	NA
Detection limit	0.016	NA
(determined according to EPA procedure pt.135, app. B)		
Carryover	0.2%	NA
Lag time	9 min	NA
Base	-16465	NA
Gain	24	NA
Lamp Intensity	58	NA

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Note: the above performance specifications were developed with the exclusive use of genuine Bran+Luebbe parts.
*Trademark of Atlas Chemical

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3. Bolleter, W.T., Bushman, C.J. and Tidwell, P.N., Anal. Chem., 33, P.592, 1961.
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6. VWPCA Methods of Chem. Anal. of Water & Wastewater, November 1969, p.137.

Rev. X 1/15/99 Bran+Luebbe USA

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Reagents

Unless otherwise specified, all chemicals should be of ACS grade or equivalent.

List of Raw Materials

Ammonium Sulfate $(NH_3)_2SO_4$) Primary Standard Grade
Brij-35, 30% Solution*
Disodium, ethylenediamine-tetracetate
Phenol, loose crystals (C_6H_5OH)
Sodium Hydroxide (NaOH)
Sodium Hypochlorite, 5% Solution (NaOCl) Commercial Grade: e.g. Clorox
Sodium Nitroprusside ($Na_2Fe(CN)_5NO.2H_2O$)
Sulfuric Acid, conc. (H_2SO_4)

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Reagent Make-Up

All water used in reagent and standard preparation must be ammonia free.

Alkaline Phenol

Phenol, loose crystals	83 g
Sodium Hydroxide, solid	48 g
Distilled Water, qs	1000 ml

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Preparation:
Add 83 g of loose crystal phenol to about 800 ml of distilled water. While cooling under tap water or in an ice bath, slowly with swirling add 48 g of sodium hydroxide. Cool to room temperature, dilute to 1000 ml with distilled water and mix thoroughly. Store in an amber glass container. This material is corrosive. Stability: Two weeks.

Sodium Hypochlorite Solution

Sodium Hypochlorite Solution, 5%	210 ml
Distilled Water, qs	500 ml

Preparation:
Dilute 210 ml of sodium hypochlorite solution 5% to 500 ml with distilled water and mix thoroughly. Prepare fresh weekly.

Sodium Nitroprusside Solution

Sodium Nitroprusside	3.5 g
Distilled Water, qs	1000 ml

Preparation:
Dissolve 3.5 g of sodium nitroprusside in about 600 ml of distilled water. Dilute to one liter with distilled water and mix thoroughly. Store in an amber container. Stability: One month.

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Disodium EDTA

Disodium EDTA	33.6 g
Sodium Hydroxide, 50% w/w	0.8 g
Distilled Water, qs	1000 ml
Brij-35	2 ml

Preparation:
Dissolve approximately 0.8 g of 50% w/w sodium hydroxide and 33.6 g of disodium EDTA in about 800 ml of distilled water. Dilute to one liter. Add 2 ml of Brij-35 and mix well.

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Standard Preparation

Stock standard A, 100 mg/L N

Ammonium Sulfate	0.4717 g
Chloroform	1 ml
Distilled Water, qs	1000 ml

Preparation:
In a one liter volumetric flask containing about 800 ml of distilled water dissolve 1 ml of chloroform. Add 0.4717 g of ammonium sulfate and swirl to dissolve. Dilute to one liter with distilled water and mix thoroughly.

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Stock Standard B. 20 mg/L N

Stock Standard A	20.0 ml
Distilled Water, qs	100 ml

Preparation:
Dilute 20.0 ml of stock standard A to 100 ml with distilled water and mix thoroughly. Prepare fresh daily.

Working Standard Solutions

ml Stock B	mg/l N
2.0	0.4
4.0	0.8
6.0	1.2
8.0	1.6
10.0	2.0
15.0	3.0

Preparation:
Transfer aliquots of Stock Standard 6 as noted above, to individual 100 ml volumetric flasks. Dilute to volume with distilled water and mix thoroughly. Prepare fresh daily.

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Sample Preparation

1. Preserve by addition of 2 ml/L H_2SO_4 and refrigerate at 4° C.
2. Sample turbidity should be removed by filtration prior to analysis. It may interfere with this chemistry.
3. Sample cups can be rinsed with 1:1 hydrochloric acid, followed by distilled water and finally by an aliquot of the sample itself.

System Cleansing Procedure

Pump 5N H_2SO_4 as the cleaning solution.

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System Performance

Maximum reagent/water baseline	0.40 AU
Reagent Equilibration time	5 min
Sensitivity of high standard at a STD CAL of 1.0	0.22 AU
Coefficient of Variation	1.2%

Flow Diagram

1. If analysis is to be performed in a contaminated environment, scrub the air with 5N H2SO4
2. Check that the appropriate harness and optical filters are secured in their proper positions.

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CONSUMMABLES

The following annual consumption rates are based on system operation 8 hours/day, 250 days/year.

Description	Part Number	Est. Annual Usage
ORN/BLU, 0.05mL/min	116-0549-03	5pkg./12
ORN/YEL, 0.16mL/min	116-0549-05	3pkg./12
BLK/BLK, 0.32mL/min	116-0549-07	5pkg./12
ORN/ORN, 0.42mL/min	116-0549-08	3pkg./12
WHT/WHT, 0.60mL/min	116-0549-09	3pkg./12
GRY/GRY, 1.00mL/min	116-0549-11	3pkg./12
GRN/GRN, 2.00mL/min	116-0549-14	3pkg./12
Tubing air bar silicone	116-0543-01	8 ft.
Tubing Kel-F, 0.050" ID	171-0745-01	3 ft.
Tubing Polyeth., 0.015" ID	562-2002-01	3 ft.
Tubing Polyeth, 0.030" ID	562-2003-01	3 ft.

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SPARES	Part Number	Recommended
AA3 Flowcell, 1.5 x 10mm	169+B040-01	1pc.
AAII Flowcell, 1.5 x15mm	199-B018-01	1pc.
AA3 Filter, 660nm	165-B044-66	1pc.
AAII Filter, 660nm	170-B070-26	1pc.
AAII Heating Bath, 7.7mL, 37°C	157-B273-03	1pc.
AA3 Heating Bath Coil, 5.37mL	169+B440-03	1pc.
5-turn mixing coil, right	170-0103-01	1pc.
5-turn mixing coil, left	170-0426-01	1pc.
10-turn mixing coil	157-0226-01	1pc.
Glass fitting, A10	116-B034-01	1pc.
Injection Fitting	116-0489-01	1pc.
Straight tube	116-G004-01	1pc.
Glass U	172-9038-01	1pc.
Glass Z	170-0204-01	1pc.
Glass tube	170-G022-01	1pc.
Glass tube with injection	170-G071-01	1pc.

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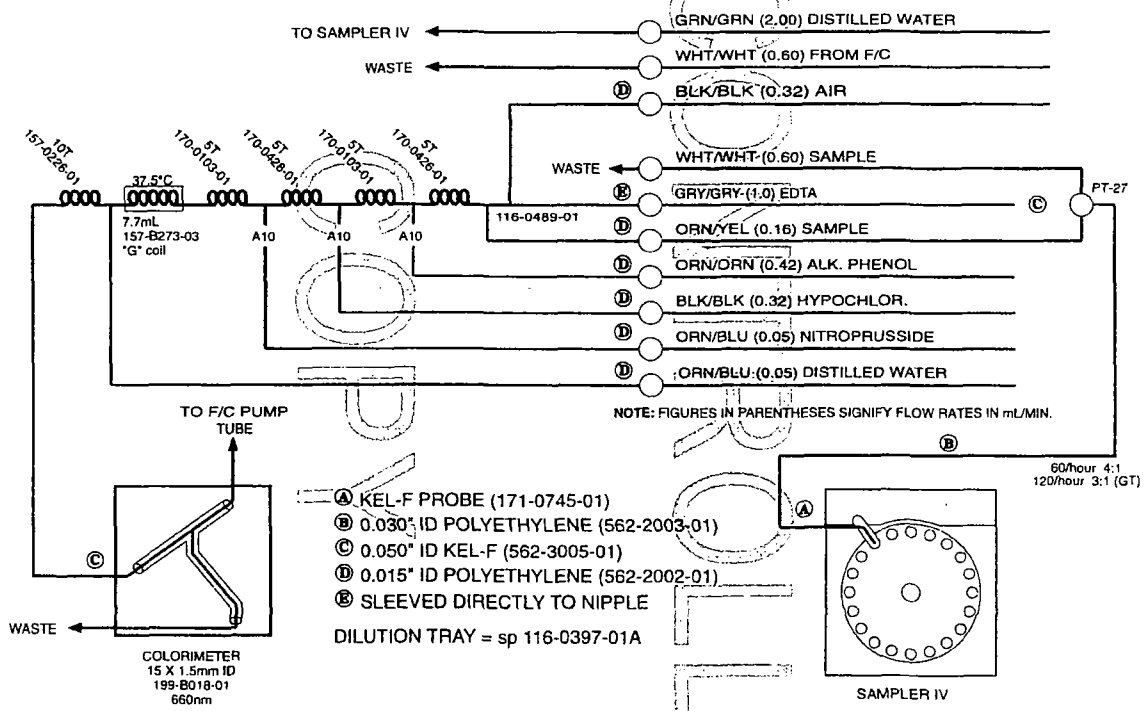
Method 696D-82W

Ammonia in water and wastewater
Manifold 116-D857-01
Harness number: 116-B346-01
Range: 0.02-3mg/L NH_3-N



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STANDARD OPERATING PROCEDURE

PHOSPHORUS DETERMINATION USING COLORIMETRIC PROCEDURE

GEN-365.3
Revision 10
August 28, 2008

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Approved By: _____ Supervisor — 8/28/08 Date

_____ QA Manager — 8-28-08 Date

_____ Laboratory Manager — 8/28/08 Date

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COLUMBIA ANALYTICAL SERVICES, INC.
1317 South 13th Avenue
Kelso, Washington 98626

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Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL
NUMBER: _____
Initials: _____ Date: _____

PHOSPHORUS DETERMINATION USING COLORIMETRIC PROCEDURE

1. SCOPE AND APPLICATION

1.1. This procedure applies to the determination of ortho, hydrolyzable and total phosphorus and is applicable to EPA method 365.3 and SM 4500P- E.

1.2. The analytical procedures detailed in this SOP are applicable to most aqueous samples. A preparative procedure is also described for determination of total phosphorus is soils and solids.

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1.3. The standard calibration range for this method is 0 to 0.7 mg/L with a 50 mm cell. This range may be extended by sample dilution, or by choosing a longer or shorter path length.

1.4. The standard Method Reporting Limit (MRL) for method 365.3 is currently 0.01 mg/L in solution for total and orthophosphorus and 0.05mg/L for method SM 4500P- F for orthophosphorus. Method Detection Limits of 0.003 mg/L orthophosphorus (365.3), 0.02mg/L orthophosphorus (SM 4500-P- E) and 0.004 mg/L total phosphorus have been achieved. The MRL in soil is 0.1 mg/kg.

2. METHOD SUMMARY

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2.1. Ammonium molybdate and Antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The intensity of the blue color is proportional to the phosphorus concentration.

2.2. Only orthophosphate forms a blue color in this test. Determination of other phosphorus forms requires a preliminary digestion step to convert other forms to orthophosphate. Sample preparation procedures for phosphorus are given in section 12.

3. DEFINITIONS

3.1. Total Phosphorus (P) - All of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure.

3.2. Total Orthophosphate (P, Ortho) - Inorganic phosphorus [$(PO_4)^{-3}$] in the sample as measured by the direct colorimetric analysis procedure.

3.3. Total Hydrolyzable Phosphorus (P, Hydro) - Phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphorus. [$(P_2O_7)^{-4}$, $(P_3O_{10})^{-5}$, etc.] plus some organic phosphorus.

3.4. Total Organic Phosphorus (P, Org) - Phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate.

3.5. Dissolved Phosphorus (P-D) - All of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure.

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3.6. Dissolved Orthophosphate (P-D, Ortho) - As measured by the direct colorimetric analysis procedure.

3.7. Dissolved Hydrolyzable Phosphorus (P-D, Hydro) - As measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates.

3.8. Dissolved Organic Phosphorus (P-D, Org) - As measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate.

3.9. The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

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3.9.1. Insoluble Phosphorus (P-I) = (P)-(P-D).

3.9.2. Insoluble Orthophosphate (P-I, Ortho) = (P, Ortho) - (P-D, Ortho).

3.9.3. Insoluble Hydrolyzable Phosphorus (P-I, Hydro) = (P, Hydro) - (P-D, Hydro).

3.9.4. Insoluble Organic Phosphorus (P-I, Org) = (P, Org) - (P-D, Org).

4. INTERFERENCES

4.1. Arsenate is determined similarly to phosphorus and should be considered when present. This interference may be eliminated by reducing the arsenic acid to arsenious acid with sodium bisulfite.

4.2. When high concentrations of iron are present low recovery of phosphorus will be obtained because iron consumes a portion of the reducing agent. The bisulfite treatment will also eliminate this interference.

4.3. Samples with extremely high organic content may deplete the available oxidant, and not digest fully with the persulfate digestion procedure. These samples may require use of the Nitric/Sulfuric acid digestion found in the 18th Edition of Standard Methods for the Examination of Water and Wastewater as method #4500-P B.

4.4. Samples that contain high levels of manganese may form permanganate during persulfate digestion. This will be indicated by a pink color in the solution. As formation of permanganate consumes some of the persulfate, reaction time should be extended to allow the permanganate to complete the oxidation of organic matter.

4.5. SM 4500-P E: Arsenates react with the molibdate reagent to produce a blue color similar to that formed with phosphate. Concentrations as low as 0.1 mg As/L interfere with the phosphate determination. Hexavalent chromium and NO2- interfere to give results about 3% low at concentrations of 1 mg/L and 10 to 15% low at 10mg/L. Sulfide (Na2S) and silicate do not interfere at concentrations of 1.0 and 10mg/L.

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5. SAFETY

5.1. All appropriate safety precautions for handling solvents, reagents and samples must be taken when performing this procedure. This includes the use of personnel protective equipment, such as, safety glasses, lab coat and the correct gloves.

5.2. Chemicals, reagents and standards must be handled as described in the CAS safety policies, approved methods and in MSDSs where available. Refer to the CAS Environmental, Health and Safety Manual and the appropriate MSDS prior to beginning this method.

5.3. This procedure involves the use of sulfuric acid. Care must be taken to prevent direct contact with concentrated these acids.

6. SAMPLE COLLECTION, CONTAINERS, PRESERVATION AND STORAGE

6.1. Sample containers may be of plastic material or of pyrex glass. Collect a minimum of 50mL of sample, preferably 500 mL, for liquid samples. For soils, collect a minimum of 10 grams.

6.2. Samples for T-Phos should be preserved by the addition of 2 ml conc. H_2SO_4 per liter.

6.3. Store samples in refrigerator at 4±2°C. Analysis for O-Phos should be performed within 48 hours. Analysis for T-Phos should be performed within 28 days. There is no holding time established for soils.

7. APPARATUS AND EQUIPMENT

7.1. Spectrophotometer with wavelength set to 650 nm for O-Phos and T-Phos by 365.3 and 880 nm for O-Phos by SM 4500-P- E.

7.2. Acid washed 150 and 250 ml beakers, 50 and 100 ml graduated cylinders, and class A pipettes.

7.3. Calibrated Eppendorf/MLA/Oxford pipettors and tips.

7.4. Hot plate for digestions and bisulfite treatment.

7.5. Analytical balance - capable of weighing to the nearest 0.0001 g.

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7.6. Top-loader balance - capable of weighing to the nearest 0.01 g.

8. REAGENTS

8.1. Method SM 4500-P E

8.1.1. Sulfuric acid, H2SO4, 5N: Dilute 70ml conc. H2SO4 to 500ml with distilled water.

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8.1.2. Potassium antimonyl tartrate solution: Dessolve 1.3715 g K(SbO)C4H4O6.1/2H2O in 400ml distilled water in a 500 ml volumetric flask and dilute to volume. Store in a glass-stoppered bottle.

8.1.3. Ammonium molybdate solution: Dissolved 20 g (NH4)6Mo7O24. 4H2O in 500 ml distilled water. Store in a glass-stoppered bottle.

8.1.4. Ascorbic acid 0.1M: Dissolve 1.76 g of ascorbic acid in 100 ml of distilled water. This solution is stable for 1 week.

8.1.5. Combined reagent: Mix the above reagents in the following proportions for 100 mm of the combined reagent : 50ml 5N H2SO4, 5 ml potassium antimonyl tartrate solution, 15 ml ammonium molybdate solution, and 30ml ascorbic acid solution. Mix after addition of each reagent. Let all reagents reach room temperature before they are mixed and mix in the order given. If turbidity forms in the combined reagent. Shake and let stand for a few minutes until turbidity disappears before proceeding. Thee reagent is stable for 4 h.

8.2. Method 365.3

8.2.1. Ammonium molybdate-antimony potassium tartrate solution: Dissolve 8 g of ammonium molybdate and 0.2 g antimony potassium tartrate in 800 ml of distilled water and dilute to 1 L. This reagent expires 6 months from date of preparation.

8.2.2. Ascorbic acid solution: Dissolve 60 g of ascorbic acid in 800 ml of distilled water and dilute to 1 L. Add 2 ml of acetone. This solution is stable for two weeks.

8.2.3. Sulfuric acid, 11 N - Slowly add 310 ml of concentrated H_2SO_4 to approximately 600 ml distilled water. Cool and dilute to 1 liter. This reagent expires 6 months from date of preparation.

8.2.4. Sodium bisulfite ($NaHSO_3$) solution: Dissolve 5.2 g of $NaHSO_3$ in 100 ml of 1.0 N H_2SO_4. This reagent expires 6 months from date of preparation.

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8.2.5. Ammonium persulfate, crystals - ACS Grade. This chemical expires 5 years from date opened.

8.2.6. Stock phosphorus solution: Dissolve 0.2196 g of predried (105°C for one hour) KH_2PO_4 in distilled water and dilute to 500 ml. 100 mg/L P. This standard expires 6 months from date of preparation.

8.2.7. Organic Phosphorus Spike (100 µg/ml - P) for total phosphorus: Dissolve 0.1180 g of Adenosine mono-phosphate (AMP) in DI water, and dilute to the mark in a 100 ml class A volumetric flask. This reagent expires 6 months from date of preparation.

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8.2.8. All prepared reagents have an expiration period of one year unless otherwise specified.

8.2.9. Reagent water: laboratory deionized water.

9. RESPONSIBILITIES

9.1. It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for data review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this SOP. This demonstration is in accordance with the training program of the laboratory. Final review and sign-off of the data is performed by the department supervisor/manager or designee.

9.2. It is the responsibility of the department supervisor/manager to document analyst training. Documenting method proficiency, as described in the SOP for Documentation of Training, is also the responsibility of the department supervisor/manager.

10. PREVENTIVE MAINTENANCE

No preventive maintenance is required other than normal glassware and apparatus cleaning.

11. PROCEDURE

11.1. Wash all glassware with 50% HCl and hot water, followed by DI.

11.2. If total or hydrolyzable phosphorus is to be determined, digest the samples as described below.

11.2.1. Total Phosphorus

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11.2.1.1 Add 100 ml of sample* to a 150 ml beaker, along with 2 ml of 11 N H_2SO_4, and ≈0.8 g of Ammonium Persulfate and several glass beads. Cover the beaker with a watch glass. Repeat for all remaining field and QC samples.

*For preparation of solid samples, place 10 g of sample and 100 mL of reagent water in the beaker and mix prior to adding the H_2SO_4 and Ammonium Persulfate.

11.2.1.2. Place the covered beakers containing the sample on a hot plate, and digest for 1-2 hours, or until a final volume of 20-30 ml is reached.

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11.2.1.3. Allow the digested samples to cool. If a precipitate forms, add additional DI and heat gently to dissolve. If the crystals do not dissolve, or if the digestate contains sediment, filter the digestate through a 0.45 µm filter, and collect the filtrate in a beaker if the bisulfite treatment is required, or a 100 ml volumetric flask or equivalent container if no bisulfite treatment is needed.

11.2.1.4. If the digestate is colored, or if metal ion interferences are suspected, treat the samples and standards by adding 10 ml of sodium bisulfite solution per 100 mls of sample and warming gently for approximately 30 minutes. Routine use of the bisulfite treatment is strongly advised. The sodium bisulfite treatment is most effective after filtering sample through a 0.45µm filter.

11.2.1.5. Transfer the digestate to a 100 ml volumetric flask or equivalent container, and dilute to the mark with DI.

11.2.2. Hydrolyzable phosphorus

11.2.2.1. Add 1 ml of H2SO4 solution (8.3) to a 50 ml sample in a 125 ml Erlenmeyer flask.

11.2.2.2. Boil gently on a pre-heated hot plate for 30-40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15-20 psi). Cool, dilute to approximately 40 ml and filter.

11.2.2.3. Treat the samples as in 11.2.1.4 and 11.2.1.5 above.

11.3. Prepare a series of standards according to the following table. Be certain to use class A volumetric glassware, and properly calibrated Eppendorf/MLA pipettors. An undeveloped standard curve is stable for one week.

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Volume of 100 mg/L O-Phos Standard. (mL)	Final Volume (mL)	Standard Conc.(mg/L)
0	100	0.00
0.01	100	0.01
0.05	100	0.05
0.10	100	0.10
0.20	100	0.20
0.50	100	0.50
0.70		0.70

Note : This standard curve expires one week from date of preparation. For method SM 4500-P E do not make the 0.01 mg/L Standard.

11.4. Calibration of Spectrophotometer

11.4.1. O-Phos and T-Phos (365.3): Transfer 50 ml of each standard into a 150 ml beaker, add 1 ml of 11 N sulfuric acid and 4 ml of molybdate-antimony potassium tartrate and mix. Add 2 ml of ascorbic acid reagent, mix, and allow to sit for five minutes to allow for full color development.

11.4.2. O-Phos (SM 4500-P E): Pipet 50ml standard into a clean, dry 150 ml beaker. Add 8.0 ml combined reagent and mix thoroughly. After at least 10 min but no more than 30 min, measure absorbance of each standard at 880 nm, using reagent water as the reference solution.

11.4.3. The calibration curve is fitted to a linear, least squares model. See Appendix A. Set the spectrophotometer to 650 nm for 365.3 and 880 nm for SM 4500-P E, and zero with DI water. Read the standards; calculate the correlation coefficient, slope

and intercept. The correlation coefficient must be ≥ 0.995. If the calibration criteria are met, analyze an LCS. If the LCS recovery is acceptable, proceed with analysis of samples. If not, determine the cause of the problem, correct it, and then recalibrate.

11.4.4. Analyze an ICB (a 0.0 mg/L standard). The result must be less than the reporting limit.

11.4.5. To verify spectrophotometer calibration, analyze an ICV for T-Phos at a concentration of 0.4 mg/L. The result must be within 10% of the true value.

11.5. Analysis of Samples

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11.5.1. 365.3 Method: Highly colored or turbid samples may require background correction. To do this, add 1:1 N sulfuric acid and Ammonium molybdate-antimony potassium tartrate reagent to a separate aliquot of sample, and read the absorbance. Subtract this absorbance from that of the sample with all reagents added, prior to final calculation. If the background is greater than 0.2-0.3 absorbance units, or greater than the sample aliquot with all reagents added, dilute the sample and redetermine the background color. Some highly turbid samples may require filtration to remove suspended matter.

11.5.2. SM 4500-P E Method: Highly colored or turbid samples may require background correction. To do this, add all reagents except ascorbic acid and potassium antimonyl tartrate, and read the absorbance. Subtract this absorbance from that of the sample with all reagents added, prior to final calculation.

11.5.3. Samples with high levels of arsenate, iron or manganese should be treated with sodium bisulfite prior to analysis. See method 365.3 for the proper procedure. Note that the bisulfite treatment should follow any filtration performed on the samples, as interfering substances may dissolve from any sediment present.

11.5.4. For 365.3: Transfer 50 ml of sample to a 150 ml beaker, and develop color as specified in 12.4.1 for the standards except that no additional acid is added to samples that have been digested for total or hydrolyzable phosphorus.

11.5.5. For O-Phos by SM 4500-P E transfer 50 ml of sample to a 150 ml beaker and add 0.05ml (1 drop) phenolphthalein indicator. If red color develops add 5N H_2SO_4 solution dropwise to just discharge the color. Add 8.0 ml combined reagent and mix thoroughly. After at least 10 min but no more than 30 min, measure absorbance of each standard at 880 nm, using reagent water as the reference solution.

11.5.6. If sample absorbance exceeds the highest standard, dilute a suitable portion of sample to 50 ml, and proceed with color development and analysis. If a dilution is

performed, add additional acid to total or hydrolyzable phosphorus samples to ensure that each 50 ml aliquot of diluted sample contains 1 ml of 11 N H_2SO_4.

12. QA/QC REQUIREMENTS

12.1. The ability of each analyst/instrument to generate acceptable accuracy and precision must be documented prior to sample analysis by performing 4 replicate LCS analyses and calculating average recovery and %RSD. Method criteria must be met for these results. This must be completed before analysis of samples, or whenever significant changes to the procedures have been made.

12.2. A method detection limit (MDL) study must be undertaken before analysis of samples can begin. The MDL studies should be done for each matrix, prep method, and instrument. Refer to the CAS SOP for The Determination of Method Detection Limits and Limits of Detection.

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12.3. Ongoing QC Samples required for each sample batch (20 or fewer samples) are described in the CAS-Kelso Quality Assurance Manual and in the SOP for Sample Batches. In general, these include:

12.3.1. Method blanks - Method Blanks are aliquots of reagent water which are carried through the same procedure as the samples. Method Blanks must not contain detectable amounts of analyte > MRL, or the samples must be rerun.

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12.4. The LCS, or laboratory control standard, is a purchased standard used to check the performance of the analytical system. The LCS recovery must be within acceptance limits before samples can be analyzed.

12.4.1. CCV's are portions of 0.5 mg/L standard which are analyzed to verify continued spectrophotometer calibration. CCV's must be within 10% of the true value (96-104% for Arizona samples), or the affected sample batch must be repeated.

12.4.2. CCB's are 0.0 mg/L standards. CCB's must be less than the reporting limit, or the affected batch must be repeated.

12.4.3. Matrix duplicates and matrix spikes must be run at a minimum of one set per batch of 20 or fewer samples. CCV/CCB pairs must be run after every 10th reading made on the spectrophotometer.

12.4.4. The relative percent difference (RPD) between matrix duplicates should be within acceptance limits. If not, the supervisor should be notified at the time of analysis, and corrective action taken as appropriate for the sample.

12.4.5. Matrix spike recovery must be within acceptance limits. If not, the sample must be checked for interferences and reanalyzed. Samples should be spiked at ~5 times the expected sample value. Spike levels may be calculated as follows.

Aqueous matrices:

$$Spike\ added = \frac{spike\ concentraction\ (mg\ /L\ )\ x\ volume\ of\ spike\ taken\ (ml\ )}{ml\ of\ sample\ used}$$

Nonaqueous matrices:

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$$Spike\ added = \frac{spike\ concentration\ (mg/L)\ x\ volume\ of\ spike\ taken\ (ml)}{g\ of\ sample\ used\ x\ \%solids(if\ applicable)}$$

Calculate percent recovery as follows:

$$Matrix\ Spike\ Recovery = \frac{Spiked\ Sample\ -\ Sample}{Spike\ Added}\ x\ 100$$

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QC Acceptance Limits						
Parameter	LCS (% Recovery)		MS (% Recovery)		RPD (%)	
	Water	Soil	Water	Soil	Water	Soil
Total Phosphorus	85-115[d]	85-115[i]	75-125[d]	75-125[i]	20[d]	20[d]
Ortho Phosphorus	85-115[d]	-	75-125[d]	-	20[d]	20[d]

[d] Default limits which are within laboratory statistical limits.

[i] Default limits – insufficient data points for determination of laboratory statistical limits.

13. DATA REDUCTION AND REPORTING

13.1. All data and corrective actions must be recorded into the bench records by the analyst. All analysis descriptions (samples, blanks, CCVs, etc.), measurements, and readings are recorded on the applicable benchsheet. The benchheet is used to document all analyses and to perform calculations leading for final sample results.

13.2. It is the analyst's responsibility to review analytical data to ensure that all quality control requirements have been met for each analytical run. Results for QC analyses are calculated and recorded as specified for samples. These results are then used to calculate QC determinations (recovery, RPD, etc.)

13.3. Following sample and QC analyses, calculate results as follows:

Water matrices:

$$mg/L\ P = \frac{mg/L\ \ standard\ curve\ x\ finalvolume(mL)}{Initial\ sample\ volume(mL)}$$

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$$Spike\ added = \frac{spike\ concentration(mg/L)\ x\ volume\ of\ spike\ taken(ml)}{ml\ of\ sample\ used}$$

Nonaqueous matrices:

$$mg/kg\ P = \frac{(mg/L\ \ curve)(Final\ Solution\ Volume)}{(Sample\ Weight, g)(\%\ Solids)}$$

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$$Spike\ Added = \frac{(Spike\ Solution\ Concentrated(mg/L))(Volume\ of\ Spike\ Added(ml))}{(Sample\ Weight, g)(\%\ Solids)}$$

13.4. The data packet for the sequence is submitted for review by supervisor or designee. The results are transferred to the appropriate report form located in the CAS network directory R:\WET\WIP. These forms are made from templates located in R:\WET\FORMS. Once the results are transferred, the report is reviewed.

13.5. Reporting results as "Orthophosphate as Phosphorus", in mg/L or mg/kg units; or for total phosphorus, "Phosphorus, Total" in mg/L or mg/kg units.

13.6. Refer to the SOP for Laboratory Data Review Process for general instructions for data review

14. CONTENGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

Corrective action measures applicable to specific analysis steps are discussed in the applicable section of this (and other applicable) SOP(s). Also, refer to the *SOP for Corrective Action* for correct procedures for identifying and documenting such data. Procedures for applying data qualifiers are described in the *SOP for Report Generation* or in project-specific requirements.

15. METHOD PERFORMANCE

This method was validated through single laboratory studies of accuracy and precision. Refer to the reference method for additional method performance data available.

The method detection limit (MDL) is established using the procedure described in the *SOP for The Determination of Method Detection Limits and Limits of Detection* (ADM-MDL). Method Reporting Limits are established for this method based on MDL studies and as specified in the CAS Quality Assurance Manual.

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16. POLLUTION PREVENTION

It is the laboratory's practice to minimize the amount of solvents and reagents used to perform this method wherever technically sound, feasibly possible, and within method requirements. Standards are prepared in volumes consistent with laboratory use in order to minimize the volume of expired standards to be disposed of. The threat to the environment from solvents and/or reagents used in this method may be minimized when recycled or disposed of properly.

17. WASTE MANAGEMENT

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17.1. The laboratory will comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions as specified in the CAS EH&S Manual.

17.2. This method uses acid. Waste acid is hazardous to the sewer system and to the environment. All acid waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the CAS EH&S Manual for details.

17.3. This method uses a base. Waste base is hazardous to the sewer system and to the environment. All waste must be neutralized to a pH of 2.5-12 prior to disposal down the drain. The neutralization step is considered hazardous waste treatment and must be documented on the treatment by generator record. See the CAS EH&S Manual for details

18. TRAINING

18.1. Refer to the *SOP for Documentation of Training* for standard procedures.

18.2. Training outline

18.2.1. Review literature (see references section). Read and understand the SOP. Also review the applicable MSDS for all reagents and standards used. Following these reviews, observe the procedure as performed by an experienced analyst at least three times.

18.2.2. The next training step is to assist in the procedure under the guidance of an experienced analyst. During this period, the analyst is expected to transition from a role of assisting, to performing the procedure with minimal oversight from an experienced analyst.

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18.2.3. Perform initial precision and recovery (IPR) study as described above for water samples. Summaries of the IPR are reviewed and signed by the supervisor. Copies may be forwarded to the employee's training file. For applicable tests, IPR studies should be performed in order to be equivalent to NELAC's Initial Demonstration of Capability.

18.3. Training is documented following the *SOP for Documentation of Training*.

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NOTE: When the analyst training is documented by the supervisor on internal training documentation forms, the supervisor is acknowledging that the analyst has read and understands this SOP and that adequate training has been given to the analyst to competently perform the analysis independently.

19. REFERENCES

19.1. EPA Method 365.3

19.2. Method 4500-P E in Standard Method for the Examination of Water and Wastewater, 20th Ed., 1998.

APPENDIX A

The calibration is determined using a linear regression that best fits the line of the X:Y pairs. The quality of the fit is determined by calculating the coefficient of determination (R^2), also called the correlation coefficient.

The line of regression is calculated as follows:

Start with the equation for a line, y = mx + b. From here the line of regression can be determined.

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$$m = \frac{n\sum(xy) - \sum x \sum y}{n\sum(x^2) - \left(\sum x\right)^2}$$

$$b = \frac{\sum y - m\sum x}{n}$$

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Where:

x = the values of the x variables.
y = the values of the y variables.
n = the number of data points.

Once the line of regression has been determined then the coefficient of determination can be calculated.

$$r^2 = \frac{\left(\sum xy - n\overline{x}\,\overline{y}\right)^2}{\left(\sum x^2 - \overline{x}\sum x\right) * \left(\sum y^2 - \overline{y}\sum y\right)}$$

STANDARD OPERATING PROCEDURE

LABORATORY BALANCE MONITORING AND CALIBRATION

ADM-BAL
Revision 1
August 7, 2008

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Approved By: _____ QA Manager, 8-7-08 Date

_____ Laboratory Director, 8/7/08 Date

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COLUMBIA ANALYTICAL SERVICES, INC.
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Annual review of this SOP has been performed and the SOP still reflects current practice.
Initials: _____ Date: _____
Initials: _____ Date: _____
Initials: _____ Date: _____

DOCUMENT CONTROL
NUMBER: _____
Initials: _____ Date: _____

LABORATORY BALANCE MONITORING AND CALIBRATION

1. PURPOSE

This SOP provides instructions for performing routine monitoring and calibration of laboratory balances. This is required in order to ensure proper operation of this equipment and to document compliance with QA program requirements.

2. APPLICABILITY

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This procedure applies to all balances used throughout the lab for any type of sample, standard, reagent, or miscellaneous weighing.

3. RESPONSIBILITIES

3.1. Balance calibration verifications are performed by the department staff where the balances are located and used. It is the responsibility of the department manager and supervisor to ensure that the balance calibration verifications are performed as specified in this SOP.

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3.2. Laboratory QA staff is responsible for coordinating periodic outside service, calibration, and cleaning. Laboratory QA staff is responsible for reviewing and maintaining the outside service certificates.

3.3. Laboratory QA staff is responsible for providing departments with calibrated reference weights. Laboratory QA staff is responsible for coordinating periodic outside calibration of the weights and reviewing/maintaining the calibration certificates.

4. APPARATUS

Reference weights - Troemner (or equivalent) 1,10, 100, 300, and 1000g; ASTM Class 2 (or Class1) or NIST Class S. Calibration is verified annually by outside metrology service. Depending on the balances in use in various departments, sets of weights are made to accommodate balance operating ranges.

5. PROCEDURE

5.1. Balance calibration verifications are required for each day the balance is used. The NELAC Quality System Standards and DoD Quality System Manual require that the balance verifications be performed *prior to use* on each day of use. The calibration verification weights must bracket the range of use.

5.2. A bound logbook is used to record all measurements. Format the logbook such that the date, initials, balance I.D., measurements, and specifications (for the 3 weights) are listed for each balance. Record each calibration verification in the logbook.

5.3. Measurement Procedures

5.3.1. Brush off the balance pan with a clean brush and check the bubble level to insure balance is leveled.

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5.3.2. Press the zero (tare) bar on the balance; make sure readout indicates balance is tared (reads zero).

5.3.3. Measure and record the three weights designated for the balance capacity and use, as listed in the logbook.

5.3.4. Record each measurement in the logbook, being careful to correctly identify the balance being monitored.

5.3.5. Remove each weight and re-zero before performing the next measurement.

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5.3.6. The criteria for the weights being measured is as follows:

Analytical balances:	±0.1% or ±0.5mg, whichever is larger*
Top-loading balances:	±0.1% **

* Unless method-specific guidance exists
** ASTM D 4753

5.4. Corrective Action for out-of-control events

5.4.1. An out-of-control situation occurs when a measurement falls outside of specific criteria. If a balance yields a measurement that is out-of-control, several steps may be taken to return the instrument to control. Initially, the technician should review recent measurements taken from the balance, and inspect the equipment to insure that it is properly functioning. It is very important to check the bubble-level located on the balance to ensure that the balance is properly leveled.

5.4.2. If inspection and/or minor adjustment of the balance do not result in a return to control, the balance should be temporarily taken out of service, either by physical removal or by disconnecting the power to the balance and identifying it as being temporarily unavailable for use. The vendor responsible for routine metrological

services should be notified and the situation described; if return to control can be accomplished with remote instruction, this is acceptable.

5.4.3. If the balance requires service from the vendor, all necessary paperwork should be performed and the balance delivered to the service vendor, preferably by CAS courier, if possible. Where sample results are jeopardized, a non-conformity and corrective action report (NCAR) should be written and reviewed by the Quality Assurance Manager, and a copy placed in the file containing all appropriate balance information.

6. RECORDS

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6.1. All measurements are to be recorded in the applicable logbook as described above. Entries into logbooks are to be performed in accordance with the *SOP for Making Entries into Logbooks and Onto Benchsheets* (ADM-DATANTRY).

6.2. All certificates of calibration provided by outside calibration service contractors will be reviewed by the QA Manager.

7. REFERENCES

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7.1. NELAC Quality Standards, 2003.

7.2. CAS-Kelso Quality Assurance Manual.

7.3. Department of Defense Quality Systems Manual for Environmental Laboratories, Version 3, January, 2006.

8. CHANGES FROM PREVIOUS REVISION

8.1. Section 5.3.6, replaced previous criteria with criteria based on analytical balance or top-loader, as per DoD QSM. Added ASTM reference.

8.2. Section 7, added ASTM reference.

8.3. Attached ASTM D4753.

ATTACHMENT

ASTM D4753

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Designation: D 4753 – 87

Standard Specification for Evaluating, Selecting, and Specifying Balances and Scales for Use in Soil and Rock Testing[1]

This standard is issued under the fixed designation D 4753; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This specification provides minimum requirements for general-purpose scales, balances, and standard masses used in soil and rock testing.

1.2 This specification provides guidance for evaluating, selecting, and specifying general purpose scales, balances, and standard masses used in soil and rock testing.

1.3 The accuracy requirements for balances and scales are specified in terms of the combined effect of all sources of error contributing to overall balance performance. The measurement of specific sources of error and consideration of details pertaining to balance construction have been intentionally avoided.

1.4 This specification does not include requirements for balances and scales that have accuracies greater than those generally required in normal soil and rock testing.

1.5 This specification does not apply to nongraduated balances.

1.6 This specification does not address the methods used to verify or quantify specific parameters dealing with balances and scales. For a description of tests used in evaluating balance performance, see NBS Handbook 44.

1.7 This specification is not intended to be used as a specification for the purchase of balances and scales.

NOTE 1—The National Bureau of Standards (NBS) and the International Organization of Legal Metrology (OIML) publish standards or practices that specify construction requirements as well as performance specifications for balances. ASTM, OIML, and NBS publish construction standards and tolerances for standard masses.

NOTE 2—The terms "mass" and "determine the mass of" are used in this standard instead of the more commonly used terms "weight" and "weigh" to comply with standard metric practice. In addition, the term "standard mass(es)" is used instead of "weight(s)" when referring to a piece of material of known specified mass used to compare or measure the mass of other masses.

2. Referenced Documents

2.1 *ASTM Standard:*

E 617 Specification for Laboratory Weights and Precision Mass Standards[2]

2.2 *National Bureau of Standards Documents:*

NBS Handbook 44 Specifications, Tolerances, and Other Technical Requirements for Weighing and Measuring Devices[3]

NBS Handbook 105-1 Specifications and Tolerances for Reference Standards and Field Standard Weights and Measures[3]

2.3 *International Organization for Legal Metrology (OIML):*

International Recommendation No. 20 Weights of Accuracy Classes E_1, E_2, F_1, F_2, M_1 from 50 kg to 1 mg[4]

International Recommendation No. 3

3. Descriptions of Terms Specific to This Standard

3.1 *accurate*—a balance is "accurate" when its performance (its indication as determined by tests made with suitable standards) conforms to the standard within the applicable tolerances and other performance requirements. Balances that fail to conform are "inaccurate".

3.2 *balance*—an instrument for determining the mass of an object by the action of gravity on the object. See *scale.*

NOTE 3—In this specification the terms balance and scale are used interchangeably as is often done. The term balance is more often used in scientific fields of application. See Note 7.

3.3 *basic condition*—a basic condition is a condition that must be met before a basic measurement for evaluating a balance can be performed.

3.4 *basic measurement (of error)*—a basic measurement for evaluating a balance is performed by (*1*) determining the change of indication of the balance when a load of known mass is added to or subtracted from any load already on the balance; and (*2*) taking the difference between the change in the indication determined and the known value of the mass.

3.5 *basic tolerance*—basic tolerances are those tolerances that are established by a particular code for a particular device under all normal tests, whether maintenance or acceptance. Basic tolerances include minimum tolerance values when these are specified. Special tolerances, identified as such and pertaining to special tests, are not basic tolerances.

3.6 *capacity—of a balance*, the maximum load recommended by the manufacturer, disregarding any additional capability supplied by a taring device.

3.7 *general-purpose balance*—any balance used to make a general purpose determination of mass. See *general-purpose determination of mass.*

[1] This specification is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.99 on Quality Control.

Current edition approved Nov. 27, 1987. Published January 1988.

[2] *Annual Book of ASTM Standards*, Vol 14.02.

[3] Available from the Superintendent of Documents, US Government Printing Office, Washington, DC 20402.

[4] Available from the International Standards, National Bureau of Standards, US Department of Commerce, Gaithersburg, MD 20899.

3.8 *general-purpose determination of mass*—a single determination of mass using a balance (not a special purpose determination of mass involving repeat determinations of mass, averages, standard deviations, corrections etc.).

3.9 *general-purpose standard mass*—a standard mass used with a balance to make a general purpose determination of mass. See *general-purpose determination of mass.*

3.10 *hysteresis*—the difference between indications obtained when the value of the applied load is reached by adding mass or by removing mass from the load receiving element of a balance.

3.11 *linearity error*—plus or minus deviation from the theoretically straight-lined (linear) course of two interdependent values. In balances, this expression is applied to the plus or minus deviation of the indicated measurement value from the true (actual) value of the load.

NOTE 4—The term linearity implies that the deviation from the true values are a continuous function of the applied load. Thus, obtaining enough values of the true applied load versus balance reading to establish a relation between applied load and output should give the error that will occur at any applied load. Linearity, then, is a statement about the systematic (nonrandom) error of a balance. Superimposed on the linearity are precision and other effects, such as off-center errors, temperature effects, etc. Linearity is a measure of balance performance over its full range, and on most balances adjustments can be made to alter the useableness of a balance with a given linearity for weighings within a particular range of use.

3.12 *nongraduated balance*—balances not fitted with a scale numbered in units of mass.

3.13 *off-center error—of a top loading or platform balance*, the difference in indicated value when a mass is shifted to various positions on the loading area (pan or platform); eccentric load error.

NOTE 5—The test for off-center error is called the shift test, or off-center-load test. Information about balance performance under eccentric loadings is not normally found in product literature but such information can usually be obtained by contacting the manufacturers directly.

3.14 *precision of a balance*—the degree of agreement between the indications of a balance for repeated determinations of mass of the same mass under essentially the same conditions. It is usually expressed quantitatively as a standard deviation of a series of weighings, or as a function of the range of several determinations of mass. See *repeatability type II, reproducibility.*

3.15 *readability type I*—the value of the smallest unit of mass that can be read without estimation over the given range of measurement either directly or by use of a vernier or micrometer.

3.16 *readability type II*—the value of the smallest unit of mass that can be read *with* estimation over the given range of measurement.

3.17 *readability type III*—the value of the smallest unit of mass that can be read while the balance is in use, but not smaller than readability Type I.

NOTE 6—Readability Type III refers to the smallest unit of mass that can be read when in-service conditions such as draft, vibration, and other environmental conditions affect the balance.

3.18 *repeatability type I*—the degree of agreement between the indications of a balance for repeated determinations of the same mass under essentially the same conditions. The degree of agreement (qualitatively).

3.19 *repeatability type II*—see *precision.*

3.20 *reproducibility*—see *precision.*

3.21 *scale*—see *balance.*

NOTE 7—The term scale usually refers to instruments intended for commercial or industrial applications, and when so used, usually implies an instrument of lesser performance than a balance.

3.22 *sensitivity*—the ratio of the deflection (ΔL) of the balance indicator or self-indicating display to the load (ΔM) causing the deflection; $S = \Delta L/\Delta M$ at a given load.

NOTE 8—Values for sensitivity are sometimes seen expressed in terms of mass units. When used in this way in reference to a non-self-indicating balance, sensitivity refers to the reciprocal of sensitivity or the change in mass required to change the position of equilibrium (rest point) a specified amount, usually one division on the balance indicator. When used in reference to self-indicating balances, it refers to the change in mass required to change the indication by one scale division.

3.23 *standard mass*—an object of specified mass and construction used with balances, and for the verification of balances and other masses.

3.24 *taring range*—a range within which it is possible to reset the display to zero by means of the tare device.

3.25 *tolerance*—a value fixing the limit of allowable error or departure from true performance or value.

NOTE 9—For additional terms used in this specification related to balances and standard masses, see NBS Handbook 44 or OIML IR No. 3.

4. Significance and Use

4.1 This specification provides those writing and using test standards related to soil and rock with a means for determining the balance capabilities required for a particular test method and for describing the balance selected in a uniform fashion.

4.2 This specification provides agencies conducting soil and rock testing with guidance for selecting and evaluating general purpose balances and standard masses.

4.3 This specification provides inspection organizations with criteria for evaluating general purpose balances and standard masses.

5. Requirements for General-Purpose Balances

5.1 General-purpose balances shall be judged accurate for a given class if their indications meet the basic tolerances shown in Table 1.

6. Requirements for General-Purpose Weights

6.1 General-purpose standard masses for use in testing of soil and rock should conform to the requirements in Specification E 617 for Type I or Type II, Grade S, O, or P standard masses and have tolerance limits equal to or better than those for Class 6 standard masses except that the maintenance tolerances given in Specification E 617 for Class 6 standard masses are to be considered acceptance tolerances for purposes of this specification and the maintenance tolerances twice those values. The tolerances given in Table 2 correspond to the minimum acceptable maintenance tolerances under this specification.

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TABLE 1 Requirements for General-Purpose Balances

Class	Test Mass,[A] g	Basic Tolerance	Readability Type I,[B] g
GP1	≥20	±0.1 %	0.01
	<20	±0.02 g	0.01
GP2	≥200	±0.1 %	0.1
	<200	±0.2 g	0.1
GP5	≥2000	±0.1 %	1
	<2000	±2 g	1
GP10	≥5000	±0.1 %	5
	<5000	±5 g	5
GP100	≥50 000	±0.1 %	50
	<50 000	±50 g	50

[A] The known mass which is added to or subtracted from any load already on the balance when making a basic measurement (of error).
[B] Not readability Type II.

NOTE 10—Former NBS Class J, M, S, S-1, P, and Q standard masses meet this specification, as do OIML Class M_1 standard masses (IR No. 20).

TABLE 2 Tolerances for General-Purpose Standard Masses

Denomination	Tolerance,[A] mg
20 kg	4000
10 kg	2000
5 kg	1000
3 kg	600
2 kg	400
1 kg	200
500 g	100
300 g	60
200 g	40
100 g	20
50 g	14
30 g	10
20 g	6
10 g	4
5 g	4
3 g	4
2 g	4
1 g	4
500 mg	2
300 mg	2
200 mg	2
100 mg	2

[A] Acceptance tolerances on new general-purpose standard masses are one-half the maintenance tolerances shown in this table.

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7. Evaluation of General-Purpose Balances

7.1 *Basic Tolerance*—Table 1 shows the basic tolerances for all classes of general-purpose balances used in soil or rock testing that are covered by this specification. The basic tolerances shown apply to basic measurements made when evaluating a balance.

7.1.1 A basic measurement for evaluating a balance is performed by determining the change of indication of the balance when a known mass is added to or subtracted from any load already on the balance, and then taking the difference between the change in the indication determined and the known value of the mass. To evaluate a balance, the basic tolerances shown in Table 1 are applied to the known value of the mass used in the basic measurement. The result of a basic measurement must fall within the error allowed by the basic tolerance.

NOTE 11—For nearly all determinations of mass encountered in soils testing, the value of interest is the difference between two determinations of mass. In cases where the difference between the two determinations of mass is small, relative to the total masses determined, it is desirable to specify a tolerance based on the difference between the two determinations of mass to relieve what might otherwise be an excessively stringent tolerance.

NOTE 12—A no load condition may be treated as a load of 0.0 g and may be considered a load on the balance.

7.1.2 The basic tolerance for a balance should apply to all values of loading within the range of the balance without regard to whether the balance is properly zeroed or a tare mass is being used, and should apply under all usual and customary methods of operation. Furthermore, the basic tolerance must be met in the environment in which the balance is to be used.

7.1.3 A balance shall not be considered acceptable if the result of basic measurements involving any combination of poise locations, counterpoise masses, pan loading, and scale positions, or unit masses are not within the basic tolerances shown in Table 1.

7.1.4 When evaluating top loading balances, results of basic measurements under off-center loading must also meet basic tolerances.

NOTE 13—The possibility of off-center error and linearity error should be considered when making basic measurements.

7.1.5 Standard masses meeting or exceeding the requirements given in Specification E 617 for weights of Type I or Type II, Grades S or O, and Class 2 are suggested in Specification E 617 for use as working standards for calibration and precision analytical work and are recommended in this specification for use in evaluating general purpose balances. The use of standard masses of lesser quality for calibration purposes is discouraged because of the tendency to think of them as accurate once they are labeled "standard masses for calibration."

7.2 *Balance Classification*—A balance is classified by reference to its readability Type I (see Table 1).

NOTE 14—Capacity is not to be considered when classifying a balance. Balance classification in this specification is based on balance performance, not on use requirements. When selecting a balance, the anticipated loads which the balance is expected to measure will dictate the capacity required.

7.3 *Basic Conditions*—A basic condition is a condition which must be met before a basic measurement for evaluating a balance can be performed. In general, basic conditions require that a balance give a clear and stable indication under any condition of loading including the indication at no load. Both the useable readability (readability Type III) and the repeatability Type I must be adequate to perform the basic measurements described in 7.1.

NOTE 15—For example, when a determination of mass is made with a beam balance, if the smallest poise is moved by an amount equal to the readability Type I, the indicating pointer must move clearly off balance (usually at least one division on the pointer scale). This is an indication of the adequacy of the sensitivity of a balance.

7.3.1 Readability Type I (not Type II) establishes the balance's class for determining the appropriate basic tolerance. If environmental or other factors cause the usable readability (readability Type III) to be poorer than the readability Type I then the balance cannot meet the basic tolerance for its class.

7.3.2 The repeatability Type I of the balance being evaluated must be such that the difference between the

highest and lowest values in a group of several determinations of mass of the same load shall not be greater than twice the balance's readability Type I.

7.4 *Balance Testing*—Three types of testing may be performed when evaluating the performance of a balance.

7.4.1 *Acceptance Testing*—Acceptance testing should be performed on new or newly repaired or reconditioned balances. The basic measurement for evaluating a balance is performed in an environment that meets the manufacturer's recommendations. An acceptance tolerance equal to or better than one-half the basic tolerance should apply to all basic measurements for this test.

7.4.2 *Maintenance Testing*—Maintenance testing should be performed on balances in service. The basic measurement for evaluating a balance is performed in an environment that meets the manufacturer's recommendations. Maintenance testing is performed to determine whether a balance should be repaired. A tolerance equal to or better than the basic tolerance should apply to all basic measurements for this test.

7.4.3 *In-Use Testing*—In-use testing should be performed on balances in service. The basic measurement for evaluating a balance should be performed as and where the balance is used to make general purpose determinations of mass. In-use tests are intended to indicate the quality of usual and customary mass determinations that are made or may be made when using a general-purpose balance. The basic tolerance should apply to basic measurements for this test.

7.5 *Rejection*—If a balance fails when in-use tests are performed then maintenance tests should be performed. If a balance fails both in-use and maintenance tests, it should be removed from service and repaired or replaced. If a balance fails the in-use test but passes the maintenance test, the environment in which the balance is located must be improved.

8. Evaluation of General-Purpose Standard Masses

8.1 General-purpose standard masses should be tested on a precision balance. Standard masses meeting or exceeding the requirements given in Specification E 617 for standard masses of Type I or Type II, Grades S or O, and Class 2 are suggested in Specification E 617 for use as working standards for calibration and precision analytical work and are recommended in this specification for use in evaluating general purpose standard masses. The use of standard masses of lesser quality for calibration purposes is discouraged because of the tendency to think of them as accurate once they are labeled "standard masses for calibration."

8.2 General-purpose standard masses that fail to meet the requirements specified in Section 6 should be removed from service and either adjusted to meet acceptance tolerances or replaced.

9. Selecting and Specifying Balances

9.1 *Selecting Balances*—The selection of a balance is based on the proposed use. A balance must have a capacity sufficient to accommodate all anticipated test loads, and its performance must be good enough so as not to be a cause of test error. The accuracy desired in test results should be used to establish the allowable balance tolerances.

9.1.1 The precision of a balance (a term frequently found in manufacturer's specifications), expressed as a standard deviation, shall not be greater than one-half the readability Type I (not Type II).

9.1.2 When listed by the manufacturer, the linearity error of a balance shall not be greater than one-half the readability Type I (not Type II).

9.1.3 If the maximum error of indication contributed by off-center loading can be obtained from the manufacturer, it should be no greater than one-half the readability Type I (not Type II).

9.1.4 In cases where a test requires that more than one test result be determined, several balances having different capabilities may be required.

NOTE 16—The following example explains how a balance is selected: assume that a test method requires that a sample of soil be graded and that the fractions be reported to the nearest 0.1 %. If the sample mass is 1000 g, then a balance having a minimum capability of determining the mass of each fraction to the nearest 1.0 g (0.1 % of the total sample mass) will be required. If the sample mass is 5000 g, then a balance having a minimum capability of determining the mass of each fraction to the nearest 5.0 g (0.1 % of the total sample mass) will be required.

9.2 *Specifying Balances*—An example of the wording that may be used to specify balances in ASTM standards is as follows:

Balance—A balance having a minimum capacity of ____ g or kg and meeting the requirements of Specification D 4753 for a balance of ____ g readability.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

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STANDARD OPERATING PROCEDURE

for

Corrective Action

SOP Code: ADM - CA

Revision: 5

September 12, 2007

Approved by: _____ Quality Assurance — 11-12-08 Date

_____ Chief Quality Officer — 11-12-08 Date

_____ President — 11-18-08 Date

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Annual review of this SOP has been performed and the SOP still reflects current practice.	DOCUMENT CONTROL
Initials: LW Date: 11-12-08	NUMBER: _____
Initials: _____ Date: _____	Initials: _____ Date: _____
Initials: _____ Date: _____	

Standard Operating Procedure for Corrective Action

1.0 PURPOSE

This standard operating procedure (SOP) describes a systematic procedure for documenting nonconforming events and problems (such as errors, deficiencies, deviations, laboratory events, or data that fall outside of established acceptance limits) and the resolution of the nonconformity event or problem (i.e., corrective action). A Nonconformity and Corrective Action Report Form is utilized to document (1) identification of the nonconformity and/or problem, (2) investigation of the causes, and (3) corrective actions taken, including, but not necessarily limited to, repetition of the test or analysis. Procedures are also described for notifying affected parties, including the CAS customer.

The overall purpose of corrective action is to improve the quality of test results to an acceptable level and to maintain the level. Corrective action is one part of a comprehensive quality assurance program that emphasizes problem or nonconformity correction. (A companion process, preventive action, described in the *SOP for Preventive Action*, emphasizes nonconformity or problem prevention.)

2.0 APPLICABILITY

All CAS employees are to be alert to identifying nonconformities and problems when errors, deficiencies, deviations, or out-of-control situations are detected. On-the-spot, remedial corrective actions routinely made by technicians and chemists should be documented as normal operating procedures, and no specific documentation need be made other than notations in laboratory maintenance logbooks, for example. This SOP establishes a formal system of reporting and documenting corrective actions for (major) nonconformities or problems that affect the quality of the results reported to our customers. Examples of nonconformities or problems requiring documentation include, but are not limited to, the following examples.

- Quality control results outside acceptance limits for accuracy and precision
- Method blanks or continuing calibration blanks (CCBs) containing contaminants above acceptable levels
- Undesirable trends in recoveries of spikes or in relative percent differences between duplicates
- Sample holding time missed
- Unacceptable results in performance evaluation samples
- Deficiencies found during internal or external system audits
- Customer inquiries concerning data quality

3.0 DEFINITIONS

3.1 Nonconformity

A nonconformity is a departure of a quality characteristic from its intended level or state severe enough to cause an associated product or service not to meet a required specification. (American National Standard ANSI/ASQC Z1.4-1981)

3.2 Causes of Nonconformities

The cause of a nonconformity is that agent, situation, or event that produces the nonconformity, error, defect, deviation, problem, or undesirable situation.

3.2.1 Chance Causes These are random, unpredictable happenings or events without apparent cause, or the apparent absence of a cause.

3.2.2 Assignable Causes (or systematic errors) The causes of a nonconformity due to a known or knowable reason; for example, an error, improper procedure, or an interference in the sample.

3.3 Remedial Action

Remedial action is what is done right away to fix the nonconformity or problem and/or what is done short-term until a real fix can be figured out.

Remedial action is the tool for fixing the *product* of a process.

3.4 Corrective Action

Corrective action is the action taken to eliminate the cause(s) of an existing nonconformity, defect, problem, or undesirable situation in order to prevent recurrence. (NELAC)

Corrective action is a process that involves (1) root cause analysis, (2) developing a corrective action plan that will prevent recurrence, (3) implementing a corrective action plan that will prevent recurrence, and (4) assessing the action taken to determine its effectiveness.[1]

Corrective action is what is done to fix the *process* so the defect won't happen again.

[1] Denise Robitaille, "Separating the 'Shalls' from the 'Shoulds', *The Auditor*, July-August, 2007, page 31

3.5 Root Cause Analysis

Root cause analysis is the process of identifying the most basic reason(s) or causal factor(s) for an undesirable condition or problem, which, if eliminated or corrected, would prevent the undesirable condition or problem from existing or recurring.

3.6 Error

Errors are a deviation from what is right and correct.

3.7 Blunder

Blunders are errors resulting from carelessness, inattention, misunderstanding, etc.

4.0 DISCUSSION

When analytical errors, deficiencies, deviations, out-of-control situations, and undesirable performance are discovered as the result of a laboratory's own quality assessment efforts, from its participation in performance evaluation sample analyses, and from internal and external systems audits, a process is needed for reporting and documenting the correction of these nonconformities or problems and improving performance.

The goal of quality assurance is error prevention, not just error correction. Accordingly, records are to be kept of nonconformities and problems and the corrective actions that are taken to alleviate them. These records are to be regularly reviewed for the effectiveness of the corrective actions as well as for any patterns or persistence of specific nonconformities or problems. CAS is committed to continually examining and improving its measurement processes.

5.0 RESPONSIBILITIES

Everyone in the laboratory has the responsibility to perform his or her job according to established specifications and procedures. Everyone has the responsibility to know when their work product does not meet the control criteria established for that activity. When nonconformities or problems or out-of-control situations occur, everyone has the responsibility to initiate the action of restoring the process to its normal functioning.

Corrective action procedures are often initiated and handled at the bench level by the technician who reviews the data produced by the entire analytical process. If the problem persists or cannot be identified by the chemist, the matter is referred to the department supervisor, laboratory manager, or the laboratory's Quality Assurance Program Manager (QA PM) for further investigation.

Laboratory management and the laboratory's QA PM are responsible to act upon Nonconformity and Corrective Action Reports (NCARs). Furthermore, laboratory managers are ultimately account-able for the follow through, verification, and evaluation of the effectiveness of corrective action(s).

The laboratory's QA PM must review all corrective actions for effectiveness and look for patterns or persistence of specific nonconformities or problems.

6.0 PROCEDURE

6.1 Nonconformity Identification

The first objective is to positively identify the kind of nonconformity or problem that is present and whether it is persistent or transitory. Determining the cause(s) of a nonconformity can be difficult. There are two kinds of causes that affect a measurement process. Chance causes occur randomly and affect precision whereas assignable causes can produce bias or unacceptable imprecision. Any technically significant nonconformity or problem should be investigated for an assignable cause. Assignable causes should be minimized or eliminated, if possible.

Table 1 is a checklist that can be used to aid in the identification of nonconformities or problems.

6.2 Corrective Action Process

6.2.1 Cause Analysis

The corrective action process begins with an investigation to determine the root cause(s) of the nonconformity or problem.

"Cause analysis is the key and sometimes the most difficult part in the corrective action procedure. Often the root cause is not obvious and thus a careful analysis of all potential causes of the problem is required. Potential causes could include customer requirements, the samples, sample specifications, methods and procedures, staff skills and training, consumables, or equipment and its calibration."[2]

Quality tools such as flowcharts, fishbone diagrams, and why-why diagrams are sometimes useful in determining the root cause of a nonconformity or problem.

The cause analysis shall be documented.

Table 2 lists examples of common remedial and corrective actions.

6.2.2 Corrective Action Plan Development

During the root cause analysis phase (Section 6.2.1), most likely one or more causes will be identified. During this phase, one or more plans may be devised

[2] Reference 9.3, Section 4.11.2

that would potentially solve and eliminate the nonconformity or problem. One specific plan will be selected and a detailed plan will be developed that will most likely eliminate the nonconformity or problem. The goal of the plan is to prevent recurrence. The plan may involve, for example, simplifying or redesigning a procedure, retraining personnel, obtaining new materials, obtaining new equipment, or other modifications, or a combination of these things.

The corrective action plan development and the selected plan shall be documented.

The plan will be communicated to and approved by the affected manager.

6.2.3 Corrective Action Plan Implementation

The plan developed in Section 6.2.2 will be implemented. The plan will be communicated to the affected personnel. To implement the corrective action plan, any necessary changes to the affected process need to be made.

The corrective action plan implementation shall be documented.

6.2.4 Corrective Action Plan Monitoring

The corrective action that was implemented (in Section 6.2.3) shall be monitored to assess its effectiveness. Monitoring may consistent of observation of what was changed, evaluation of data (such as control charts), internal audits, etc.

If the corrective action does not eliminate the nonconformity or problem or it is not as effective as desired, it may be necessary to go back (a) to the cause analysis (Section 6.2.1) because the root cause was not identified or (b) to the corrective action plan development (Section 6.2.2) because the plan was flawed for some reason or (c) to the corrective plan implementation (Section 6.2.3) because the plan wasn't being followed, for example.

The corrective action plan monitoring shall be documented.

6.2.5 Corrective Action Closure

Closure of the corrective action is completed when the implemented corrective action eliminates the nonconformity or problem and the SOP for the process has been revised, approved, and implemented.

6.3 Documentation

A Nonconformity and Corrective Action Report (NCAR) is used to (1) document identification and details of the nonconformity, problem, or out-of-control situation; (2) describe the corrective action(s) taken; and (3) provide documentation of approval and customer notification (if necessary). The following instructions are for the NCAR form on page 15. Other NCAR formats may be used as long as the essential components and information are present.

6.3.1 Nonconformity

This section of the NCAR is used to document the details of the nonconformity, problem, or out-of-control situation.

6.3.1.1 NCAR Number This is a number that is assigned to make each NCAR unique and to permit tracking it. A suggested format is *yy-nnn*, where *yy* is a two-digit designation for the year and *nnn* is a three-digit counter starting with 001 for the first NCAR of the year.

6.3.1.2 Procedure (SOP or Method) Indicate the analysis or activity involved. For example, sulfate analysis by Method 300.0.

6.3.1.3 Event Date Record the date the nonconformity occurred or was identified.

6.3.1.4 Event Check the box next the description of the nonconformity. If none of the listed events are appropriate, check the Other box and describe the event.

6.3.1.5 Samples/Projects/Customers/Systems Affected List the samples, projects, customers, and/or systems affected by the nonconformity, problem or out-of-control situation. If samples are involved, list the lab codes of all the affected samples.

6.3.1.6 Detailed Description Describe the nonconformity, problem, or out-of-control situation in detail.

6.3.1.7 Originator and Date Fill in the name of the person initiating the NCAR and the date it was prepared.

6.3.1.8 Project Manager, Notified by, and Date The Project Manager(s) is(are) to be notified of the nonconformity, problem, or out-of-control situation at this point in the process. Fill in the name of the Project Manager(s)

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who was(were) notified, who did the notifying, and the date the Project Manager(s) was(were) notified.

6.3.2 Corrective Action and Outcome

This section of the NCAR is used to describe in detail the corrective action and the result. Before corrective action is taken, an investigation into the root cause should be done.

6.3.2.1 Root Cause Analysis Corrective action should start with an investigation to determine the root cause (Section 6.2) of the nonconformity identified in Section 6.1.

6.3.2.2 Corrective Action and Outcome Use this part of the Report to describe in detail what corrective actions were taken to restore the system to acceptable performance. Corrective actions need to focus on (1) **fixing** the particular nonconformity (remedial action) and on (2) **preventing** the nonconformity from ever happening again by correcting the root cause (corrective action). The result of the corrective action should also be described (i.e., was the corrective action effective and satisfactory?). For example:

Nonconformity: Sample refrigerator temperature too high, above 6° C.
Remedial Action: Repairman called in who cleaned the cooling coils.
Corrective Action: Regular maintenance will include cooling coil cleaning.
Outcome: Temperature restored to 4° C. within 8 hours. Thermostat was not adjusted.

6.3.2.3 Corrective Actions for Out-of-Control Data This subject is addressed in analysis-specific SOPs in a Section with the same title. See Reference 9.5.

6.3.2.4 Is the data to be flagged in the Analytical Report with an appropriate qualifier? If the sample results are to be reported in spite of the nonconformity, whether or not an appropriate qualifier is to be added onto the results needs to be determined and noted.

6.3.3 Approval and Notification

This section of the NCAR is used to document verification and approval of the corrective action(s). Customer notification of the nonconformity and corrective action is also documented.

6.3.3.1 Supervisor Verification and Approval The supervisor of the person responsible for performing the corrective action(s) verifies, approves, signs, and dates the Report indicating that the corrective action taken is acceptable. The supervisor may add comments.

6.3.3.2 QA PM Verification and Approval The laboratory's QA PM verifies, approves, signs, and dates the Report indicating that the corrective action taken is acceptable. The QA PM may add comments.

6.3.3.3 Customer Notification The appropriate box is checked by the Project Manager.

6.3.3.4 Project Manager Verification and Approval The Project Manager(s) for the affected samples, projects, and/or customers verifies, approves, signs, and dates the Report indicating that the corrective action taken is acceptable. The Project Manager also needs to retain records of pertinent customer communications. The Project Manager may add comments.

6.3.4 Filing

6.3.4.1 Samples/Projects/Customers The original NCAR is placed in the project file with the original raw data. If more than one service request is involved, the service request or project file containing the original NCAR is noted on the original NCAR and photocopies are placed in the other files. A photocopy of the NCAR is returned to the supervisor of the department affected by the nonconformity. Another photocopy of the NCAR is given to the QA PM to be filed in a corrective action file.

6.3.4.2 Systems The original NCAR is filed with the appropriate system, job, or client file. For example, an NCAR for a sample cooler problem would be filed with the daily temperature check logbook or with the sample cooler maintenance file. A photocopy of the NCAR is given to the QA PM for filing in a corrective action file.

6.4 Audit Findings

Audit findings, from either internal or external audits, are normally written out in some sort of an audit report by the assessor. To document and track corrective actions to the findings from audits, the Audit Finding Response Form on page 16 may be used.

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6.4.1 Audit Information In this top section of the Form, indicate who is to address the finding, the location where the finding was observed (e.g., which department), the date of the audit, a reference of some sort so that the finding and its corrective action can be tracked to completion, and the name of the assessor.

6.4.2 Finding Identification by Assessor Indicate the specific QA system or SOP to which the finding pertains. For the description of the finding, copy the finding from the assessor's report. Either the lab's QA PM or the assessor may make a recommendation of how the finding could be corrected.

6.4.3 Corrective Action by Laboratory In this section, either
(a) describe the corrective action that was taken to correct the finding and to prevent its reoccurrence and attach evidence that the corrective action has been implemented; or
(b) describe a plan for correcting the finding with a target completion date.

Eventually, a description of the corrective action will be filled in. The supervisor affected by the finding needs to verify and approve the corrective action and sign and date.

6.4.4 Corrective Action Approval Both the laboratory's QA PM and manager need to verify and approve the corrective action and sign and date.

6.5 Unacceptable Performance Testing (PT) Results

An unacceptable PT result is actually a nonconformity and as such it is to be treated as described in this SOP starting with a cause analysis (Section 6.2.1). The following list of checks may be helpful in determining the root cause.

- Check for typos or transcription errors, including if the PT vendor used the submitted result.
- Check for a calculation error.
- Check to make sure the right units were used.
- Check if there is an error associated with a dilution, either a wrong dilution was done or a wrong dilution was used in the calculation.
- Check batch QC (namely, the method blank, the LCS, the MS, and the duplicate, DLCS, or DMS) if these results were acceptable or if there was some sort of a trend or out-of-control result that would have an impact.
- Check the analytical sequence (namely, the calibration, CCBs, CCVs, etc.) if these results were acceptable or if there was some sort of trend.
- Check the analytical sequence for possible carry-over cross contamination.
- Check for process or procedure errors.

It is important to evaluate if the root cause for an unacceptable PT result is also occurring with the analysis of customers' samples.

The Performance Testing Report Form on page 17 may be used to document the investigation and corrective actions.

7.0 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

The QA PM is responsible for maintaining a file containing all completed NCARs. NCARs should be reviewed periodically by the QA PM for patterns or persistence of specific problems. The CAS Chief Quality Officer will review NCAR summary information provided in the Quarterly QA Report to Management prepared by each laboratory's QA PM.

8.0 RECORDS

8.1 A record of the identification of the nonconformity (from Section 6.1) needs to be made.

8.2 The entire correction action process (from Section 6.2) needs to be documented.

8.3 NCARs are to be archived per the instructions in Section 6.3.4.

8.4 Completed Audit Finding Response Forms (Section 6.4) are to be archived with the audit report.

8.5 A record of the results of the investigation into the cause of unacceptable PT results (Section 6.5) is to be archived with the PT report.

9.0 REFERENCES

9.1 2003 National Environmental Laboratory Accreditation Conference (NELAC) Quality Systems Standard. See Appendix A for pertinent text copied from the Standard.

9.2 Department of Defense *Quality Systems Manual for Environmental Laboratories*, Final Version 3, January 2006. See Appendix A for pertinent text copied from the *Manual.*

9.3 ISO/IEC 17025:2005(E), "General Requirements for the Competence of Testing and Calibration Laboratories." See Appendix B.

9.4 *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1998, Method 1020 B, Quality Control, Section 14.

9.5 *SOP for Preparation of SOPs*, SOP Code ADM – SOP, Section 6.3.3.16: Corrective Actions for Out-of-Control Data

10.0 CHANGES FROM PREVIOUS REVISION

☆	Cover Page and title on Page 2	SOP title changed
∘	Section 1.0	First sentence revised; second paragraph revised
☆	Section 3.3	New term; subsequent Sections renumbered
∘	Section 3.4	Second and third paragraphs are new
•	Section 4.0	Revised; former Section 4.1 moved to new Section 6.1; second paragraph is formerly Section 4.2
•	Section 6.0	First paragraph moved to Section 6.3
•	Section 6.1	Formerly Section 4.1
★	Section 6.2	New section
•	Section 6.3	Formerly first paragraph in Section 6.0; paragraph revised to include point numbering in first sentence
•	Section 6.3.1	Formerly Section 6.1
•	Section 6.3.1.8	Project Chemist changed to Project Manager
•	Section 6.3.2	Formerly Section 6.2
•	Section 6.3.2.2	In the example, "Corrective Action" changed to "Remedial Action" and "Long-term" changed to "Corrective Action"
•	Section 6.3.3	Formerly Section 6.3
∘	Section 6.3.4	Formerly Section 6.5
★	Section 6.5	New section
★	Section 8.0	All new
•	Reference 9.1	Updated
•	Reference 9.2	Updated
•	Reference 9.3	New
★	NCAR Form on Page 15	Updated
★	Performance Testing Report Form on Page 17	New
•	Appendix A	New
•	Appendix B	New

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TABLE 1

Deficiency Correction Checklist

Possible Problem		A	B
Procedural Change		*	*
Sampling		*	
Sample Handling		*	
Analytical Procedure:	Calculations	*	*
	Data	*	*
	Reagents		*
	Equipment		*
	Calibration		*
	Maintenance		*
	Methodology	*	*
Blunder		*	*

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A = The measurement process is in control, but the results are questioned or are questionable.

B = The measurement process is out-of-control.

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TABLE 2

Examples of Common Remedial and Corrective Actions

QC Activity	Example Acceptance Criteria	Example Remedial and Corrective Actions
Initial Instrument Blank	Instrument response < MDL	Prepare another blank. If same response, determine cause of contamination: reagents, environment, instrument or equipment failure, etc.
Initial Calibration Standards	Correlation coefficient ≥0.995; %RSD < 20	Reanalyze standards. If still unacceptable, remake standards and reanalyze.
Initial Calibration Verification Standard (ICV)	± 15% of expected value	Reanalyze ICV. If still unacceptable, remake and reanalyze initial calibration standards. If still unacceptable, use new primary standards to make new calibration standards and recalibrate.
Continuing Calibration Verification Standards (CCV)	± 15% of expected value	Reanalyze standard. If still unacceptable, recalibrate and reanalyze samples from last acceptable CCV.
Method Blank	≤ MDL or <MRL	Reanalyze the method blank. If still unacceptable, determine source of contamination. If necessary, reprocess the batch of samples.
Laboratory Control Sample (LCS)	±10% of expected value	Reanalyze LCS. If still unacceptable, reprocess the batch of samples.

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Nonconformity and Corrective Action Report

CAS

NONCONFORMITY

NCAR No. _____

PROCEDURE (SOP or METHOD): EVENT DATE: _____

EVENT: ☐ Missed Holding Time ☐ QC Failure ☐ Lab Error (spilled sample, spiking error, etc.)
☐ Method Blank Contamination ☐ Login Error ☐ Project Management Error
☐ Equipment Failure ☐ Unacceptable PT Sample Result
☐ SOP Deviation ☐ Other (describe):

SAMPLES / PROJECTS / CUSTOMERS / SYSTEMS AFFECTED

PROPRIETARY

DETAILED DESCRIPTION

ORIGINATOR: _____ DATE: _____

PROJECT MANAGER(S): _____ NOTIFIED BY: _____ DATE: _____

AND

CORRECTIVE ACTION AND OUTCOME

Re-establishment of conformity must be demonstrated and documented. Describe the steps that were taken, or are planned to be taken, to correct the particular Nonconformity and prevent its reoccurrence. Include Project Manager instructions here.

Is the data to be flagged in the Analytical Report with an appropriate qualifier? ☐ No ☐ Yes

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APPROVAL AND NOTIFICATION

Supervisor Verification and Approval of Corrective Action _____ Date: _____
Comments:

QA PM Verification and Approval of Corrective Action _____ Date: _____
Comments:

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Customer Notified by ☐ Telephone ☐ Fax ☐ E-mail ☐ Narrative ☐ Not notified
Project Manager Verification and Approval of Corrective Action _____ Date: _____
Comments:

(Attach record or cite reference where record is located.)

COPY

AUDIT FINDING RESPONSE FORM

To: _____ Location: _____ Audit Date: _____

Finding Reference: _____ Assessor: _____

FINDING IDENTIFICATION BY ASSESSOR

QA System or SOP Affected: _____

Description of Finding: _____

The following action is recommended to correct this finding and prevent recurrence: _____

CORRECTIVE ACTION BY LABORATORY

Describe the corrective action that was taken to correct this finding and to prevent recurrence and attach evidence that the corrective action has been implemented.
<<Alternatively, describe a plan for correcting the finding with a target completion date.>>

Proposed By: _____ Date: _____

Supervisor Verification and Approval of Corrective Action: _____ Date: _____

CORRECTIVE ACTION APPROVAL

The corrective action taken is Acceptable / Not Acceptable.

QA PM Verification and Approval of Corrective Action: _____ Date: _____

Lab. Mgr Verification and Approval of Corrective Action: _____ Date: _____

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Performance Testing Report

PT Study [fill in study number]

Laboratory's Response to "Not Acceptable" Result

PT Sample:	
Method Description:	
Analyte:	
Reported Value:	
Assigned Value:	
Acceptance Limits:	
NCAR Reference:	

Response: (Description of laboratory's investigation and corrective actions.)

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Quality Assurance Program Manager Date

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Appendix A
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2003 NELAC Standard (Reference 9.1) and the DoD Quality Systems Manual (Reference 9.2)

Control of Nonconforming Environmental Testing Work (NELAC Section 5.4.9; DoD Section 4.9)

.1 The laboratory shall have a policy and procedures that shall be implemented when any aspect of its environmental testing work, or the results of this work, do not conform to its own procedures or the agreed requirements of the client. The policy and procedures shall ensure that:

a) the responsibilities and authorities for the management of nonconforming work are designated and actions (including halting of work and withholding of test reports, as necessary) are defined and taken when nonconforming work is identified;

b) an evaluation of the significance of the nonconforming work is made;

c) corrective actions are taken immediately, together with any decision about the acceptability of the nonconforming work;

d) where the data quality is or may be impacted, the client is notified; and

e) the responsibility for authorizing the resumption of work is defined.

.2 Where the evaluation indicates that the nonconforming work could recur or that there is doubt about the compliance of the laboratory's operations with its own policies and procedures, the corrective action procedures given in [NELAC 5.4.10; DoD 4.10] shall be promptly followed.

Corrective Action (NELAC Section 5.4.10; DoD Section 4.10)

.1 General

The laboratory shall establish a policy and procedure and shall designate appropriate authorities for implementing corrective action when nonconforming work or departures from the policies and procedures in the quality system or technical operations have been identified.

.2 Cause Analysis

The procedure for corrective action shall start with an investigation to determine the root cause(s) of the problem.

.3 Selection and Implementation of Corrective Actions

Where corrective action is needed, the laboratory shall identify potential corrective actions. It shall select and implement the action(s) most likely to eliminate the problem and to prevent recurrence. Corrective actions shall be to a degree appropriate to the magnitude and the risk of the problem. The laboratory shall document and implement any required changes resulting from corrective action investigations.

.4 Monitoring of Corrective Actions

The laboratory shall monitor the results to ensure that the corrective actions taken have been effective.

.5 Additional Audits

Where the identification of nonconformances or departures casts doubts on the laboratory's compliance with its own policies and procedures, or on its compliance with this Standard, the laboratory shall ensure that the appropriate areas of activity are audited in accordance with 4.13 as soon as possible.

.6 Technical Corrective Action

a) In addition to providing acceptance criteria and specific protocols for corrective actions in the Method SOPs (see 5.4.1.1), the laboratory shall implement general procedures to be followed to determine when departures from documented policies, procedures and quality control have occurred. These procedures shall include but are not limited to the following:

1) identify the individual(s) responsible for assessing each QC data type;

2) identify the individual(s) responsible for initiating and/or recommending corrective actions;

3) define how the analyst shall treat a data set if the associated QC measurements are unacceptable;

4) specify how out-of-control situations and subsequent corrective actions are to be documented; and

5) specify procedures for management (including the quality manager) to review corrective action reports.

DoD QSM Clarification Box 19:
Audits – Corrective Action: Managers, including the quality manager, are also responsible for acting upon corrective action report reviews. Furthermore, managers are ultimately accountable for the follow through, verification, and evaluation of these corrective actions.

Monitoring of Corrective Actions: Historical corrective action reports should be periodically reviewed to identify long-term trends or recurring problems.

Regular Review: All operations shall be systematically and thoroughly reviewed at regular intervals (at least annually) to:

- Obtain input on the laboratory's operations:
- Determine what considerations need to be given to input (from reviews); and
- Determine how corrective action(s), if necessary, shall be carried out.

Reference: American Society for Quality Control. 1991. Q2 – Quality Management and Quality System Elements for Laboratories – Guidelines.

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Appendix B
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ISO/IEC 17025:2005(E) Standard (Reference 9.3)

4.11 Corrective action

4.11.1 General

The laboratory shall establish a policy and a procedure and shall designate appropriate authorities for implementing corrective action when nonconforming work or departures from the policies and procedures in the management system or technical operations have been identified.

NOTE A problem with the management system or with the technical operations of the laboratory may be identified through a variety of activities, such as control of nonconforming work, internal or external audits, management reviews, feedback from customers, and from staff observations.

4.11.2 Cause analysis

The procedure for corrective action shall start with an investigation to determine the root cause(s) of the problem.

NOTE Cause analysis is the key and sometimes the most difficult part in the corrective action procedure. Often the root cause is not obvious and thus a careful analysis of all potential causes of the problem is required. Potential causes could include customer requirements, the samples, sample specifications, methods and procedures, staff skills and training, consumables, or equipment and its calibration.

4.11.3 Selection and implementation of corrective actions

Where corrective action is needed, the laboratory shall identify potential corrective actions. It shall select and implement the action(s) most likely to eliminate the problem and to prevent recurrence.

Corrective actions shall be to a degree appropriate to the magnitude and the risk of the problem.

The laboratory shall document and implement any required changes resulting from corrective action investigations.

4.11.4 Monitoring of corrective actions

The laboratory shall monitor the results to ensure that the corrective actions taken have been effective.

4.11.5 Additional audits

Where the identification of nonconformities or departures casts doubts on the laboratory's compliance with its own policies and procedures, or on its compliance with this International Standard, the laboratory shall ensure that the appropriate areas of activity are audited in accordance with 4.14 as soon as possible.

NOTE Such additional audits often follow the implementation of the corrective actions to confirm their effectiveness. An additional audit should be necessary only when a serious issue or risk to the business is identified.