Remedial Planning Activities at Selected Uncontrolled Hazardous Waste Sites in Region III

Contract No. 68-W8-0090
ALTERNATIVE REMEDIAL CONTRACTING STRATEGY PROGRAM
SAMPLING AND ANALYSIS PLAN
SALTVILLE RI/FS OVERSIGHT

EPA CONTRACT NO. 68-W8-0090
EPA WORK ASSIGNMENT NO.: 90-09-3L24
CH2M HILL PROJECT NO. WDC63107.PP.QS

Prepared for:
U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION III
841 Chestnut Street
Philadelphia, Pennsylvania 19107

Prepared by:
CH2M HILL
Reston, Virginia

April 1990
April 12, 1990

WDC63107.PP.QS

Mr. Paul Leonard  
U.S. Environmental Protection Agency Region III  
841 Chestnut Street  
Philadelphia, Pennsylvania 19107

Dear Mr. Leonard:

Subject: Submittal of Saltville RI/FS Oversight Sampling and Analysis Plan

Enclosed are 2 copies of CH2M HILL's revised sampling and analysis plan (SAP) for the Saltville RI/FS field oversight activities. The SAP has been revised to address the comments contained in the conditional approval letter dated March 1, 1990, from Claudia Walters/CRL to you.

Each of the comments has been addressed in the SAP with the exception of one question. On page 6a of the letter, Claudia asks how long it will take for the PRP to homogenize the samples in their lab. The PRP has not provided this information. We will revise the SAP to include this information when it is provided, if you so direct us.

The addition of data validation of the first batch of data will require a change in our work plan budget. We will be preparing a WPRR to reflect this cost.

Please feel free to call me in our Reston office at (703) 471-1441 or Sadia Kissoon in our San Francisco office, (temporarily) at (415) 652-2426, if you have any questions.

Sincerely,

CH2M HILL

Nelline K. Scheuer, P.E.  
Environmental Engineer  
Field Coordinator

Enclosures  
WDCC8/168.51  
cc: Claudia Walters/EPA CRL w/Enclosure (3 copies)
<table>
<thead>
<tr>
<th>No.</th>
<th>Reviewed by</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CH2M HILL's SM</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>CH2M HILL's Designated QC Manager</td>
<td></td>
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<tr>
<td>3.</td>
<td>EPA Region III's RPM</td>
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<td>4.</td>
<td>EPA Region III Central Regional Laboratory</td>
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<tr>
<td>5.</td>
<td>Brooks Rand, Ltd. Analytical Laboratory PM</td>
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<td>6.</td>
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</table>

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DISTRIBUTION LIST

No. of Copies

EPA Region III

Jerry Curtin/PO
Paul Leonard/RPM
Claudia Walters/Central Regional Laboratory

CH2M HILL

Bob Dagostaro/ARCS PM
Sadia Kissoon/SM
Skip Ellis/RI/FS QC Manager/RTL

WDCR436/003.50
FOREWORD

This Sampling and Analysis Plan (SAP) is written for oversight remedial investigation (RI) activities to be conducted at the Saltville Waste Disposal Site. The SAP consists of three parts:

1. The Quality Assurance Project Plan (QAPjP)--The QAPjP describes the policy, organization, functional activities, and quality assurance (QA) and quality control (QC) protocols necessary to achieve Data Quality Objectives (DQOs) dictated by the intended use of the data.

2. The Field Sampling Plan (FSP)--The FSP provides guidance for all fieldwork by defining in detail the sampling and data-gathering methods to be used during field activities.

3. The Health and Safety Plan (HSP)--The HSP for the field effort describes CH2M HILL's health and safety program for RI field activities. The HSP identifies potentially hazardous operations and exposures and prescribes appropriate protective measures.

WDCR436/004.50
Quality Assurance Project Plan
ALTERNATIVE REMEDIAL CONTRACTING STRATEGY PROGRAM
QUALITY ASSURANCE PROJECT PLAN (QAPJPP)
SALTVILLE RI/FS OVERSIGHT

EPA CONTRACT NO. 68-W8-0090
EPA WORK ASSIGNMENT NO: 90-09-3L24
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Reston, Virginia

April 1990
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# ACRONYMS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tr>
<td>ARCS</td>
<td>Alternative Remedial Contracting Strategy</td>
</tr>
<tr>
<td>ASM</td>
<td>ARCS Sample Manager</td>
</tr>
<tr>
<td>CA</td>
<td>Corrective Action</td>
</tr>
<tr>
<td>CLP</td>
<td>Contract Laboratory Program</td>
</tr>
<tr>
<td>COC</td>
<td>Chain-of-Custody</td>
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<tr>
<td>DQO</td>
<td>Data Quality Objective</td>
</tr>
<tr>
<td>DV</td>
<td>Data Validator</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>FC</td>
<td>Field Coordinator</td>
</tr>
<tr>
<td>FS</td>
<td>Feasibility Study</td>
</tr>
<tr>
<td>FSP</td>
<td>Field Sampling Plan</td>
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<tr>
<td>HSP</td>
<td>Health and Safety Plan</td>
</tr>
<tr>
<td>MCL</td>
<td>Maximum Contaminant Level</td>
</tr>
<tr>
<td>MS</td>
<td>Matrix Spike</td>
</tr>
<tr>
<td>NFHR</td>
<td>North Fork Holston River</td>
</tr>
<tr>
<td>NPL</td>
<td>National Priorities List</td>
</tr>
<tr>
<td>P</td>
<td>Percent Recovery</td>
</tr>
<tr>
<td>PID</td>
<td>Photoionization Detector</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PRP</td>
<td>Potentially Responsible Party</td>
</tr>
<tr>
<td>QA</td>
<td>Quality Assurance</td>
</tr>
<tr>
<td>QAPjP</td>
<td>Quality Assurance Project Plan</td>
</tr>
<tr>
<td>QC</td>
<td>Quality Control</td>
</tr>
<tr>
<td>QCM</td>
<td>Quality Control Manager</td>
</tr>
<tr>
<td>RAS</td>
<td>Routine Analytical Service</td>
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<tr>
<td>RI</td>
<td>Remedial Investigation</td>
</tr>
<tr>
<td>ROD</td>
<td>Record of Decision</td>
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<tr>
<td>RPD</td>
<td>Relative Percent Difference</td>
</tr>
<tr>
<td>RPM</td>
<td>Remedial Project Manager</td>
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<tr>
<td>RSD</td>
<td>Relative Standard Deviation</td>
</tr>
<tr>
<td>RTL</td>
<td>Review Team Leader</td>
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<td>SAP</td>
<td>Sampling and Analysis Plan</td>
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<tr>
<td>SAS</td>
<td>Special Analytical Service</td>
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<td>SC</td>
<td>Sample Collectors</td>
</tr>
<tr>
<td>SDWA</td>
<td>Safe Drinking Water Act</td>
</tr>
<tr>
<td>SM</td>
<td>Site Manager</td>
</tr>
<tr>
<td>SMO</td>
<td>Sample Management Office</td>
</tr>
<tr>
<td>SOW</td>
<td>Statement of Work</td>
</tr>
</tbody>
</table>
SPM - Sample Processing Manager
VASWCB- Virginia State Water Control Board
µg/l - Micrograms per liter

WDCR436/007.50
Environmental Protection Agency (EPA) policy requires all Alternative Remedial Contracting Strategy (ARCS) activities to be under the control of a centrally managed Quality Assurance (QA) program. This program is defined in the Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA, October 1988, for hazardous waste site investigations. This requirement applies to all environmental monitoring and measurement efforts mandated by or supported by EPA.

Each investigator has the responsibility to implement procedures to determine that the precision, accuracy, completeness, representativeness, and comparability of their data are known and documented. In addition, the investigator should specify acceptable quality levels for data. To meet this responsibility uniformly, each investigator must have a written QA Project Plan (QAPjP) covering each project that is investigated.

The QAPjP is prepared by EPA Region III and CH2M HILL. The QAPjP presents, in specific terms, the policies, objectives, organization, functional activities, and QA and quality control (QC) activities designed to achieve the data quality goals of the specific project. Where possible, existing QA/QC guidelines, policies, programs, and other specifics are incorporated into the QAPjP by reference.
PROJECT DESCRIPTION

PROJECT BACKGROUND AND SITE HISTORY

The Saltville Waste Disposal Site, shown in Figure 2-1, is located along the North Fork Holston River (NFHR). This former plant site is situated between the town of Saltville and the community of Allison Gap in western Smyth County, Virginia; the waste ponds extend southwest of the plant site and into Washington County, Virginia.

From 1951 to 1972, the potentially responsible party (PRP) operated an electrolyte chlorine and caustic soda plant at the Saltville site. One of the electrodes used in the chlorine-caustic process contained mercury, which was released into the process wastes and onto the plant grounds. Waste Pond No. 5 was used to dispose of the waste sludges from the chlor-alkali processes. In 1963, Waste Pond No. 6 was constructed to receive overflow from Waste Pond No. 5. According to the PRP, no wastes containing mercury were dumped into Waste Pond No. 6, but structural components of the old chlor-alkali plant reportedly were buried at the eastern edge of the pond.

The Superfund site includes the former chlor-alkali plant and the two waste ponds described above. Contamination has reportedly migrated into the NFHR, which flows adjacent to the southern border of the site and southwest into Tennessee.

A task force of representatives from EPA Region III, the Virginia State Water Control Board (VASWCB), the Tennessee Valley Authority, and the Tennessee Department of Public Health was organized in 1970 to study the mercury contamination. The task force also served as a board of advisors to the VASWCB.

The site was proposed for the National Priorities List (NPL) in 1982. In September 1982, the PRP and the VASWCB signed a Special Order, wherein the PRP agreed to perform remedial actions to remove mercury from the river. The actions,
which were completed by 1983, were to dredge 1,000 feet of the river, spread the dredged sediments onsite, and cap the area. The PRP also constructed a diversion ditch, surrounding the western portion of Waste Pond No. 5. The Special Order also required monitoring of the outfall and fish and sediments in the NFHR until 1988.

Region III completed a preliminary risk assessment in September 1986 using the data collected under the VASWCB Special Order. Additional remedial investigations were not performed. Based on the results of the preliminary risk assessment, an interim Record of Decision (ROD) was signed in June 1987. This ROD also required that a remedial investigation/feasibility study (RI/FS) be conducted which would:

- Define the hydrogeology of the area
- Define the extent of the area acting as the source of contamination to quantify the amount of mercury that can leach into the groundwater and hence into the NFHR
- Sample potentially contaminated areas at the site
- Perform a bioassessment of the NFHR
- Perform a risk assessment using historic and new RI data
- Conduct an FS to determine remedial alternatives for final cleanup

EPA has separated this investigation into two operable units. Operable Unit 2 is site soil, waste, and groundwater. Operable Unit 3 is the surrounding environment to be studied in the bioassessment.
CURRENT PROJECT STATUS SUMMARY

A Consent Order was signed on September 30, 1988, stating that the PRP will conduct the RI/FS in accordance with the ROD of June 1987. The PRP's work plans for conducting the Operable Units 2 and 3 RI/FSs were approved by EPA on September 22, 1989. CH2M HILL will provide periodic oversight of field sampling activities and will collect and analyze a specified number of splits of the PRP samples.

PROJECT OBJECTIVES

The overall objectives of the RI/FS, as described in the ROD, are as follows:

- Implement a groundwater study
- Implement a bioassessment of the NFHR
- Conduct additional sampling along the NFHR
- Conduct a risk assessment to evaluate potential health hazards

CH2M HILL OVERSIGHT OBJECTIVES

The objectives of the oversight activities covered in this QAP/jP are to assess the comparability of a subset of the PRP's data with data from an independent laboratory through the analysis of split samples. This is to be done as a check of the PRP's analytical results.

SPECIFIC OBJECTIVES

In order to assess the comparability of the PRP's data, CH2M HILL will:

- Observe PRP sampling activities
- Collect and analyze splits of a specified number of PRP samples
The data from each half of a split will ultimately be compared and the results presented in a report to EPA Region III. The decision to validate data from CH2M HILL's split half of a sample will be made by EPA Region III based on the degree of discrepancy between the split and corresponding original sample results.

**QAPjP OBJECTIVES**

The objectives of the QAPjP are to specify procedures to obtain samples that are precise, accurate, complete, representative and comparable, as well as to specify sampling and analytical procedures that will permit identification of the compounds of concern.

**SCOPE OF FIELD ACTIVITIES**

The total numbers of samples to be collected by medium are provided in Table 2-1. The procedures for sample collection and custody are detailed in the Field Sampling Plan (FSP).

Sampling is scheduled to commence January 1990 and be conducted periodically, as defined in CH2M HILL's work plan, through February 1991.

Field measurements will include total mercury monitoring. Laboratory analysis will be done for total mercury and methyl mercury through a subcontract laboratory.

Table 2-1 is a summary of the Sampling and Analysis Program. Table 2-2 is an example of the sampling and preservation requirements for samples.
<table>
<thead>
<tr>
<th>Media</th>
<th>Analysis</th>
<th>Target Detection Limits</th>
<th>Proposed Analytical Method</th>
<th>Source of Analysis</th>
<th>No. of Samples</th>
<th>Field Blank</th>
<th>Replicate</th>
<th>QA/QC Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>Total Mercury</td>
<td>0.2 µg/l</td>
<td>7470</td>
<td>CLP Laboratory</td>
<td>40&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1/day</td>
<td>1/10 or at least 1/sampling event</td>
<td>Matrix spike (Double volume per 10 samples or at least each sampling event)</td>
</tr>
<tr>
<td>Soil</td>
<td>Total Mercury</td>
<td>0.10 µg/gm</td>
<td>7471&lt;sup&gt;b&lt;/sup&gt;</td>
<td>CLP Laboratory</td>
<td>3</td>
<td>None</td>
<td>None</td>
<td>NBS or NRC standards per 10 samples*. Matrix spike for total mercury.</td>
</tr>
<tr>
<td>Waste</td>
<td>Total Mercury</td>
<td>0.25 µg/gm</td>
<td>7471&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Subcontract Laboratory</td>
<td>2</td>
<td>None</td>
<td>None</td>
<td>NBS or NRC standards per 10 samples*. Matrix spike for total mercury.</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>0.10 µg/gm</td>
<td>7471&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Subcontract Laboratory</td>
<td>2</td>
<td>None</td>
<td>None</td>
<td>NBS or NRC standards per 10 samples*. Matrix spike for total mercury.</td>
</tr>
<tr>
<td>Fish</td>
<td>Methyl Mercury</td>
<td>0.25 µg/gm</td>
<td>Bloom&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Subcontract Laboratory</td>
<td>40-60&lt;sup&gt;d&lt;/sup&gt;</td>
<td>None</td>
<td>1/10 or at least 1/sampling event</td>
<td>NBS or NRC standards per 10 samples*. Matrix spike for total mercury.</td>
</tr>
<tr>
<td>Macr.vertebrates</td>
<td>Methyl Mercury</td>
<td>0.25 µg/gm</td>
<td>Bloom&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Subcontract Laboratory</td>
<td>10&lt;sup&gt;d&lt;/sup&gt;</td>
<td>None</td>
<td>1/10 or at least 1/sampling event</td>
<td>NBS or NRC standards per 10 samples*. Matrix spike for total mercury.</td>
</tr>
<tr>
<td>Mussels</td>
<td>Methyl Mercury</td>
<td>0.25 µg/gm</td>
<td>Bloom&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Subcontract Laboratory</td>
<td>20&lt;sup&gt;d&lt;/sup&gt;</td>
<td>None</td>
<td>1/10 or at least 1/sampling event</td>
<td>NBS or NRC standards per 10 samples*. Matrix spike for total mercury.</td>
</tr>
</tbody>
</table>

*Split samples are not being collected from the bioaccumulation study samples.

<sup>a</sup>Digestion step of SW-846 7471 may be modified.


<sup>c</sup>One split to 20 samples collected by FRP.

<sup>d</sup>Duplicate samples will be submitted only if adequate volume is available.

*National Bureau of Standards (NBS) or National Research Council (NRC) of Canada certified standards for methyl mercury.
### Table 2-2
SAMPLE AND PRESERVATION REQUIREMENTS

<table>
<thead>
<tr>
<th>Media</th>
<th>Measurement</th>
<th>Amount Required</th>
<th>Container</th>
<th>Preservative</th>
<th>Holding Time</th>
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<tr>
<td>Groundwater</td>
<td>Total Mercury</td>
<td>1000 ml</td>
<td>P</td>
<td>HNO₃ to pH §2</td>
<td>28 days</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cool, 4°C</td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>Total Mercury</td>
<td>6 oz.</td>
<td>G</td>
<td>None, 4°C</td>
<td>28 days</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>6 oz.</td>
<td>G</td>
<td>None, 4°C</td>
<td>28 days</td>
</tr>
<tr>
<td>Waste</td>
<td>Total Mercury</td>
<td>6 oz.</td>
<td>G</td>
<td>None, 4°C</td>
<td>28 days</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>6 oz.</td>
<td>G</td>
<td>None, 4°C</td>
<td>28 days</td>
</tr>
<tr>
<td>Fish</td>
<td>Total Mercury</td>
<td>3 oz.</td>
<td>G</td>
<td>None, Frozen</td>
<td>28 days</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>3 oz.</td>
<td>G</td>
<td>None, Frozen</td>
<td>28 days</td>
</tr>
<tr>
<td>Macroinvertebrates</td>
<td>Total Mercury</td>
<td>3 oz.</td>
<td>G</td>
<td>None, Frozen</td>
<td>28 days</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>3 oz.</td>
<td>G</td>
<td>None, Frozen</td>
<td>28 days</td>
</tr>
<tr>
<td>Mussels</td>
<td>Total Mercury</td>
<td>3 oz.</td>
<td>G</td>
<td>None, Frozen</td>
<td>28 days</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>3 oz.</td>
<td>G</td>
<td>None, Frozen</td>
<td>28 days</td>
</tr>
</tbody>
</table>

*Amount required is the amount necessary for a single analysis. Additional volumes required for laboratory quality assurance samples (replicates, spikes).§1-liter polyethylene bottles (P) or glass (G). Eight-oz. acid-washed glass jars with teflon liners for sediments and soils, 4-oz. jars for biological samples.*
PROJECT ORGANIZATION

The project team organization for the oversight of the RI field sampling effort is shown in Figure 3-1. The responsibilities of key members of the project team are discussed below.

Primary responsibility for project quality rests with the EPA Remedial Project Manager (RPM) and the CH2M HILL site manager (SM). Independent QA review is provided by senior technical reviewers and QA auditors. Table 3-1 shows the responsible personnel for specific QA tasks and Table 3-2 is an example list of the name, address, and telephone numbers of key project personnel.

Site Manager (SM)

The SM will be responsible for project execution. She will be responsible for all technical, financial, administrative, and agency-related aspects of the project. The SM will also select properly trained and qualified personnel. The SM will be the primary contact between CH2M HILL and the RPM.

Review Team

A QC Review Team has been organized to meet the specific technical needs of the project. The program manager will provide overall assurance that all work is performed in accordance with the ARCS III Management Plan. The Review Team Leader (RTL) will coordinate the review team and will be involved in all technical aspects of the project.

Field QC Manager

The Field QC Manager reviews and advises on all aspects of QA/QC related to sample collection and shipping. Responsibilities include:

- Conducting field audits during execution of the program
- Auditing sample custody to determine if procedures specified in the SAP are followed
- Issuing corrective action orders when necessary
<table>
<thead>
<tr>
<th>QA Task</th>
<th>Responsible Organization/Personnel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall management</td>
<td>- EPA Region III/PO</td>
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<td>- EPA Region III/RPM</td>
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<tr>
<td></td>
<td>- CH2M HILL/QC Manager</td>
</tr>
<tr>
<td></td>
<td>- CH2M HILL SM</td>
</tr>
<tr>
<td>Preparation of QAPjP and supporting documents</td>
<td>- CH2M HILL</td>
</tr>
<tr>
<td>Review and approval of QAPjP and supporting documents</td>
<td>- EPA Region III/RPM</td>
</tr>
<tr>
<td></td>
<td>- EPA Region III/CRL</td>
</tr>
<tr>
<td></td>
<td>- CH2M HILL QC Manager</td>
</tr>
<tr>
<td></td>
<td>- CH2M HILL SM</td>
</tr>
<tr>
<td>QA review and approval of reports, SOPs, field activities, auditing of</td>
<td>- CH2M HILL QC Manager</td>
</tr>
<tr>
<td>reports, procedures, internal corrective action</td>
<td>- CH2M HILL QC Manager</td>
</tr>
<tr>
<td></td>
<td>- EPA Region III/CRL</td>
</tr>
<tr>
<td>Evidence audits of field records</td>
<td>- CH2M HILL SM</td>
</tr>
<tr>
<td>Approval of QA procedures for other than CLP-RAS</td>
<td>- EPA Region III/RPM</td>
</tr>
<tr>
<td>Approval of QA Plan for field sample collection and measurements</td>
<td>- CH2M HILL SM</td>
</tr>
<tr>
<td>Approval of field sample collection activities</td>
<td>- CH2M HILL SM</td>
</tr>
<tr>
<td>Field laboratory analysis and documentation procedures</td>
<td>- CH2M HILL ARCS Sample Manager</td>
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<tr>
<td>Subcontractor laboratory oversight</td>
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</tbody>
</table>

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### Table 3-2
#### QA PROJECT PERSONNEL

<table>
<thead>
<tr>
<th>Role</th>
<th>Name</th>
<th>Address</th>
<th>Phone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site Manager</td>
<td>Sadia Kissoon</td>
<td>CH2M HILL P.O. Box 4400 Reston, VA 22090</td>
<td>703-471-1441</td>
</tr>
<tr>
<td>RI/FS QC Manager/RTL</td>
<td>Skip Ellis</td>
<td>CH2M HILL P.O. Box 4400 Reston, VA 22090</td>
<td>703/471-1441</td>
</tr>
<tr>
<td>ARCS Sample Manager</td>
<td>Tom McLaughlin</td>
<td>CH2M HILL P.O. Box 4400 Reston, VA 22090</td>
<td>703/471-1441</td>
</tr>
<tr>
<td>Subcontractor Project Manager</td>
<td>Nicolas Bloom</td>
<td>Brooks Rand, Ltd. Environmental Sciences Division 3950 Sixth Avenue Northwest Seattle, WA 98107 206/632-6017</td>
<td></td>
</tr>
<tr>
<td>Subcontractor QA Manager</td>
<td>Nicolas Bloom</td>
<td>Brooks Rand, Ltd. Environmental Science Division 3950 Sixth Avenue Northwest Seattle, WA 98107 206/632-6017</td>
<td></td>
</tr>
</tbody>
</table>

WDCR436/012.50
Analytical QC Manager

The Analytical QC Manager reviews and advises on all aspects of QA/QC related to samples analysis. Responsibilities include:

- Auditing that field analytical QA procedures are as specified in the QA/QC program
- Conducting laboratory audits during execution of the program
- Making QC evaluations and, if necessary, submitting audit samples to assist in reviewing QA/QC procedures; making recommendations to the SM concerning repeat samples and analysis if problems are detected
- Auditing sample custody to determine if procedures specified in the QAP are being followed

Field Coordinator (FC)

The FC will schedule and coordinate all CH2M HILL field activities. The FC will be responsible for the coordination and implementation of all field activities associated with the sampling and for adherence to all QA/QC procedures outlined in the Sampling and Analysis Plan (SAP). These responsibilities include:

- Verifying that field personnel are trained and qualified in sampling procedures and field analytical procedures, prior to taking samples
- Verifying that field personnel are aware of the field sampling schedule and will be available when the activity is to occur
- Participating in the field sampling quality audits with the field QC manager

Field Personnel

Field oversight personnel oversee collection of groundwater, fish, mussels, macroinvertebrates, soil, and waste samples and will collect groundwater split samples. Split samples of the other media will be obtained after homogenization of
at the PRP's laboratory. The field personnel will be under the direction of the FC. The field personnel will be responsible for the following:

- Collecting and labeling the samples following the procedures outlined in the FSP
- Taking photographs of the sampling locations and wells
- Completing all necessary documentation
- Packing and shipping the samples
- Verifying that samples are collected, labeled, preserved, stored, transported, and when necessary, filtered as specified in the SAP
- Checking that all sample documentation (labels, field notebooks, chain-of-custody (COC) records, packing lists) is correct and transmitting that information with the samples to the analytical laboratory

Because the split samples of the fish, mussels, and macroinvertebrates will be obtained by CH2M HILL after homogenization at the PRP's laboratory, a representative from CH2M HILL will be there to initiate the COC protocols and to label, pack, and ship the samples.

ARCS Sample Manager (ASM)

The primary responsibility of the ASM will be processing the samples and the analytical data. The ASM will perform the following duties:

- Coordinate with EPA Region III for the delivery of sample containers and appropriate paperwork for sample collection, custody, and shipping
- Schedule through EPA Region III for analytical laboratory services by a subcontract laboratory
- Process analytical results and present the results in tabular format for the final report

Data Validator (DV)

As directed by EPA Region III, data will be validated only if a significant discrepancy is identified between the analytical results of the original and the corresponding split sample. In the event that data validation is
required, the DV will be responsible for conducting a systematic review of the analytical data for compliance with the established QA/QC criteria based on the spike (where appropriate), duplicate, and blank results provided by the laboratory. The DV will also evaluate data accuracy, precision, sensitivity, and completeness; investigate holding times; and determine data usability.
The Data Quality Objective (DQO) development process involves three stages, including (1) definition of the question or decision to be made, (2) clarification and precise identification of the information required, and (3) data collection program design.

The purpose of collecting split sample data is to determine whether the data from the PRP laboratory are comparable to that obtained from the CH2M HILL subcontract laboratory (for methylmercury) or the CLP laboratory (for total mercury). A specified number of split samples will be collected for analysis by the CH2M HILL subcontract laboratory. The DQO for this project is to obtain data of sufficient quality for purposes of comparison with the PRP's data. Critical sample locations and other site-specific information can be found in the PRP's SAP.

The following parameters are indicators of the data quality: accuracy, precision, completeness, representativeness, and comparability. Table 4-1 summarizes the quantitative goals for the data quality indicator parameters. These parameters will be determined by QC measures taken in the field and in the laboratory. Field activities will be assessed by blanks and replicates, and laboratory activities will be subject to Sample Management Office (SMO) compliance screening. Frequencies of QC measures are shown in Table 4-2 and are described in detail in Section 10.

4.1 ACCURACY AND PRECISION

Accuracy is a measure of the agreement between an experimental determination and the true value of the parameter being measured. Analytical accuracy can be determined using known reference materials or matrix spikes (MS). Spiking of reference materials into the actual sample matrix is the preferred technique because it quantifies the effects of the matrix on the analytical accuracy. Accuracy can be expressed as the percent recovery (P) as determined by the following equation:

\[ P = \frac{SSR - SR}{SA} \times 100 \]

where:
- SSR = spiked sample result
- SR = sample result (native)
- SA = spike added
### Table 4-1

**PRECISION, ACCURACY, AND COMPLETENESS OBJECTIVES**

<table>
<thead>
<tr>
<th>Media</th>
<th>Parameter</th>
<th>Precision (Relative Percent Difference)</th>
<th>Accuracy (Percent Spike Recovery)</th>
<th>Completeness (Percent)</th>
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</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>Total Mercury</td>
<td>≤ ±20</td>
<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>≤ ±20</td>
<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td>Soil</td>
<td>Total Mercury</td>
<td>≤ ±20</td>
<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>≤ ±20</td>
<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td>Waste</td>
<td>Total Mercury</td>
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<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>≤ ±20</td>
<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td>Fish</td>
<td>Total Mercury</td>
<td>≤ ±20</td>
<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>≤ ±20</td>
<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td>Macroinvertebrates</td>
<td>Total Mercury</td>
<td>≤ ±20</td>
<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>≤ ±20</td>
<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td>Mussels</td>
<td>Total Mercury</td>
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<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>≤ ±20</td>
<td>80-120</td>
<td>85</td>
</tr>
<tr>
<td>Media</td>
<td>Analysis</td>
<td>Field Blank</td>
<td>Field Replicate&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Additional Volume Needed for MS&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
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<td>-------------</td>
<td>-----------------------------------------------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>Groundwater</td>
<td>Total Mercury</td>
<td>1/day</td>
<td>1/10 samples or at a minimum 1/sample event</td>
<td>Double volume per 10 samples</td>
</tr>
<tr>
<td>Soil</td>
<td>Total Mercury</td>
<td>None</td>
<td>None</td>
<td>Double volume per 10 samples</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>None</td>
<td>None</td>
<td>NBS or NRC standard</td>
</tr>
<tr>
<td>Waste</td>
<td>Total Mercury</td>
<td>None</td>
<td>None</td>
<td>Double volume per 10 samples</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>None</td>
<td>None</td>
<td>NBS or NRC standard</td>
</tr>
<tr>
<td>Fish</td>
<td>Total Mercury</td>
<td>None</td>
<td>1/10 samples or at a minimum 1/sample event</td>
<td>Double volume per 10 samples</td>
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<td></td>
<td>Methyl Mercury</td>
<td>None</td>
<td>1/10 samples or at a minimum 1/sample event</td>
<td>NBS or NRC standard</td>
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<tr>
<td>Macroinvertebrates</td>
<td>Total Mercury</td>
<td>None</td>
<td>1/10 samples or at a minimum 1/sample event</td>
<td>Double volume per 10 samples</td>
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<tr>
<td></td>
<td>Methyl Mercury</td>
<td>None</td>
<td>1/10 samples or at a minimum 1/sample event</td>
<td>NBS or NRC standard</td>
</tr>
<tr>
<td>Mussel</td>
<td>Total Mercury</td>
<td>None</td>
<td>1/10 samples or at a minimum 1/sample event</td>
<td>Double volume per 10 samples</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>None</td>
<td>1/10 samples or at a minimum 1/sample event</td>
<td>NBS or NRC standard</td>
</tr>
</tbody>
</table>

<sup>a</sup>Duplicates will only be collected if there is available sample volume.

<sup>b</sup>National Bureau of Standards (NBS) or National Research Council (NRC) of Canada certified standards will be used instead of the MS for methyl mercury.
Precision is the measure of the agreement or repeatability of a set of replicate results obtained from repeat determinations made under the same conditions. The precision of a duplicate determination can be expressed as the relative percent difference (RPD), which is determined by the following equation:

$$\text{RPD} = \frac{|X_1 - X_2|}{X_1 + X_2} \times 200$$

where:  
$X_1 = \text{first duplicate value}$  
$X_2 = \text{second duplicate value}$

For a given laboratory analysis, the replicate RPD values are tabulated, and the mean and standard deviation of the RPD are calculated. Control limits for precision are usually plus or minus two standard deviations from the mean.

Accuracy and precision will be monitored by using field replicate and MS samples. These data alone cannot be used to evaluate accuracy and precision of individual samples but will be used to assess the long-term accuracy and precision of the analytical method.

4.2 COMPLETENESS

Completeness is defined as the percentage of analytical measurements made that are judged to be valid, validity being defined by the DQOs. Percent completeness is calculated as the number of valid analyses divided by the total number of analyses performed times 100. As a guide, the Contract Laboratory Program (CLP) data has been found, on a nationwide basis, to be 80 to 85 percent complete. The 85 percent completeness goal has been selected here to best fulfill the DQOs.

4.3 REPRESENTATIVENESS

Representativeness expresses the degree to which sample data accurately and precisely represent parameter variations at a sampling point. Representativeness is a measure of how closely the measured results reflect the actual distribution and concentration of certain chemical compounds in the medium sampled. The FSP describes the procedures to be used to collect samples. This process will generate samples that are as representative as possible. Documentation of laboratory procedures and of field procedures as described in the FSP will be used to establish that protocols have been followed and that sample identification and integrity have been maintained.
4.4 COMPARABILITY

Comparability is the term that describes the confidence with which one data set can be compared with another. Comparability refers to such issues as using standard field and analytical techniques and reporting data in the same units. This criterion becomes important if more than one field team is collecting samples or more than one laboratory is analyzing the samples.

Separate laboratories will analyze the samples from the Saltville site. The laboratory analyzing the methyl mercury samples for the PRP will use a method that is different from the method recommended for use by the subcontract laboratory on the split samples as given in Exhibit C of Appendix A. This method, developed by Bloom, is more sensitive than the method being used by the PRP and will be continuously calibrated for accuracy by analyzing methyl mercury performance standards. In comparing results from the two data sets, the Bloom method results should have the greater accuracy. For total mercury, the PRP's laboratory and a CLP laboratory will use the methods described in Appendix D.

4.5 DETECTION LIMITS

The detection limits for total mercury and methyl mercury analysis are listed in Table 2-1. The Bloom method selected for methyl mercury is more sensitive than the method selected by the PRP, and its actual detection limit will be lower than the 0.25 μg/gm listed in Table 2-1.
Section 5
SAMPLE COLLECTION PROCEDURES

The detailed description of sampling procedures are reported in the FSP. Procedures are included which describe, at a minimum:

- Sampling point selection
- Collection of background samples
- Sample packing, handling, and shipment (including time considerations and field filtration procedures)
- Special conditions for sample container preparation and time requirements (tabulated)
- Preparation and use of trip blanks and field blanks
- Documentation of sampling activities (field forms, logbooks, photologs to record sample history, sampling conditions, and sample analyses to be conducted)
- Decontamination of personnel and equipment
- Disposal of investigation-derived wastes

A summary of the samples to be collected is shown by Table 2-1, and sample and preservation requirements are shown in Table 2-2.

WDCR436/014.50
Section 6
SAMPLE CUSTODY

The project-specific procedures for sample custody are described fully in Section 3.0 of the FSP.

A required part of any sampling and analytical program is maintaining the integrity of the sample, from sample collection to data reporting. This includes the ability to trace the possession and handling of samples from the time of collection, through analysis and final disposition. This documentation is referred to as "chain-of-custody" (COC). The essential components of this chain are summarized below:

FIELD CUSTODY

For groundwater samples, the field oversight personnel are responsible for the care and custody of samples until they are delivered (or shipped) to the laboratory custodian. Split samples of other media will be obtained after homogenization at the PRP's laboratory. CH2M HILL personnel will be present in the laboratory to assume custody and initiate the appropriate COC protocols.

TRANSFER OF CUSTODY

The COC form is to be completed before samples are shipped. The person involved in relinquishing and receiving the samples will sign, date, and note the time of sample receipt on the COC form. The first such transfer may occur between the field sampler and the sample carrier. Another transfer may occur between the sample carrier and the laboratory sample custodian. Each sample shipment will be accompanied by a COC record, which identifies the contents of the shipment.

LABORATORY CUSTODY

A custodian at the subcontract or CLP laboratory will verify that the custody seals on the sample shipment or the containers are intact and that the information on the COC matches the actual contents. Any anomalies, such as broken bottles, elevated temperatures, and missing labels, will also be noted by the laboratory custodian. The laboratory will retain sample identification tags, data sheets, original instrument output records, and logbooks, as part of the final evidence file. The laboratory's chain-of-custody SOPs are shown by the laboratory's Statement of Work (SOW).
SAMPLE DISPOSAL

Unless specifically instructed to the contrary, the analytical laboratory will be responsible for disposing of unused sample portions in accordance with RCRA regulations after the analyses have been completed and any outstanding issues between the contractor and the laboratory have been resolved. Special instructions are described in the FSP.

DATA SUBMITTAL BY THE LABORATORY

All data will be submitted to meet the specific requirements for data submitted for analyses as stated in the analytical SOW to the subcontract laboratory. The SOW is shown in Appendix A.

FINAL EVIDENCE FILE

The laboratory is required to retain and deliver to CH2M HILL all materials pertaining to the sample and its analysis in the format and time-frame specified in the SOW (Appendix A).

WDCR436/015.51
A mercury meter will be used during oversight of fieldwork and collection of groundwater samples, as part of the health and safety program.

7.1 FIELD EQUIPMENT CALIBRATION

The mercury meter will be calibrated prior to and during each day's use in accordance with procedures and schedules outlined in Appendix B--Gold Film Mercury Vapor Analyzer, Calibration Procedure. If an individual suspects an equipment malfunction, the device shall be removed from service, tagged so that it is not inadvertently used, and the ARCs equipment manager notified so that a substitute piece of equipment can be used. Available backup equipment will used in the event of a malfunction.

Equipment that fails calibration or becomes inoperable during use shall be removed from service and either segregated to prevent inadvertent use or tagged to indicate that it is out of calibration. Such equipment shall be repaired and satisfactorily recalibrated. Equipment that cannot be repaired will be replaced.

7.2 LABORATORY CALIBRATION

The subcontract laboratory and CLP laboratory are responsible for their own equipment and instrument calibration and maintenance. Manufacturer's guidance should be followed for general upkeep. The laboratory is also required to comply with calibration criteria specified in the SOW (Appendix A).
Section 8
ANALYTICAL PROCEDURES

Samples collected during the course of the investigation will be analyzed by a subcontract or CLP laboratory. Laboratory analysis will be done for total mercury and methyl mercury.

Table 2-1 is a summary of the Sampling and Analysis Program.

Table 2-2 is a summary of the sampling and preservation requirements for samples. Methyl mercury will be analyzed using the Bloom method as described in the analytical SOW (Appendix A). The analytical procedures for total mercury are SW-846 Method 7470 or 7471, using the recommended QC contained in these methods. The SAS requests for the total mercury analyses are included as Appendix D.
DATA REDUCTION, VALIDATION, AND REPORTING

Data reduction, validation, and reporting are steps in the overall management and use of both field and laboratory data. Figure 9-1 presents a flow chart indicating the transfer of information and flow of sample tracking forms.

DATA REDUCTION

DEFINITION

Data reduction frequently includes computation of summary statistics and their standard errors, confidence intervals, test of hypothesis relative to the parameters, and model validation. Statistically acceptable procedures shall be implemented.

Data reduction procedures specific for the methods employed in the analysis of total and methyl mercury are given in Appendix A and by reference to the SOW for Inorganic Analysis (revision of 7/88).

DATA COLLECTION

The data collected at the site will include sample location and notes regarding compliance of the PRP's sample collectors with the PRP's SAP. These data will be recorded in log books.

DATA USAGE

The data generated at the site and/or in the laboratory will be used to satisfy the individual task requirements. The equations and the typical calculation sequence that is followed to reduce the data to the acceptable format will be described in the final report for the work assignment.

BACKGROUND DATA

Background data produced for internal records and not reported as part of the analytical data include the following: laboratory worksheets, laboratory notebooks, sample tracking system forms, instrument logs, standards records, maintenance records, calibration records, and associated QC. These sources will be available for inspection during audits and for determining the validity of data.
Figure 9-1
FLOW OF FORMS AND SAMPLE AND ANALYSIS INFORMATION
Saltville Waste Disposal Site
Saltville RI/FS Oversight

CH2M HILL Field Oversight Personnel

CH2M HILL Representative at PRP Laboratory

CH2M HILL Subcontract Laboratory (for Methyl Mercury) or CLP Laboratory (for Total Mercury)

CH2M HILL Sample Manager

COC Forms

Copies of COC Forms

Field Notebooks

COC Forms

Copies of COC Forms

CH2M HILL Data Validator (As directed by EPA-III)

Electronic Data Base

Hardcopy Files

COC Forms Data Package Field Notebooks

Analytical Results

Analytical Results and Data Package
DATA VALIDATION

All of the data contained in the first package of data from CH2M HILL's split half of the samples will be validated. A subset of all the other data packages will be validated. The decision on which data to validate will be made by EPA Region III based on the degree of discrepancy between the split and corresponding original sample results. CH2M HILL will conduct the validation of the data in accordance with Region III General Guidance for Data Review, June 1988, and the most current version of the EPA document—Laboratory Data Validation, Functional Guidelines for Evaluating Inorganics Analysis.

Region III will be contacted to verify that the most current version is being used prior to conducting the data validation. The data validation staff will be familiar with the Saltville RI/FS Oversight project, its objectives, and the intended use of the data. A data validation report using the format specified by the Region will be prepared.

The following items will be reviewed to validate the data:

- Sampling procedures employed at site
- Sample holding times
- Documentation that the analytical results are within the control limits
- Documentation that data and calculations were checked by the supervisor who was not involved in the performance of sampling, analysis, or data reduction
- Documentation that a final review of the data was made by the laboratory manager for correctness and validity of the data
- Calibration of methods and instruments
- Routine instrument checks (noise levels, drift, linearity, etc.)
- Documentation on traceability of instrument standards, samples, and data
- Documentation on analytical methodology and QC methodology
- Results of performance audits with appropriate audit materials
Control for interference contaminants in analytical methods (use of reference blanks and check standards for method accuracy precision)

Documentation of routine maintenance activity to ensure analytical reliability

Documentation sample preservation and transport

Documentation of inventory control of chemicals and items used for testing, e.g., shelf life

REPORTING

CONTENTS OF REPORT

As stated in Appendix A, the laboratory must follow package format of the CLP Statement of Work for Inorganic Analysis. As a minimum, the laboratory report will contain the following information for samples:

- Title and Location of the Project
- Project Identification Number
- Name of the Report
- Date Report was Prepared
- Name, Address, and Telephone Number of the Subcontractor
- Sample Identification Number
- Name and Location of Sample
- Type of Sample (water, soil, waste, air)
- Date on which analysis was performed
- Any special observations, circumstances or comments that may be relevant for interpretation of the data
- Signature by the laboratory manager

Each parameter tested will include the following: name of parameter, EPA or other approved testing procedure references, results of analysis, and the units of the reported results. The specific report and data deliverable
requirements for the subcontract laboratory are provided in Appendix C.

**RECORDS**

The following is a description of the records to be monitored for the project:

- Records will be maintained in accordance with the requirements of this section and be kept accessible to the EPA until such time as those records are turned over to the EPA for storage.
- The records to be generated are specified in the FSP.
- Record of field activities will support the integrity of samples shall be entered on bound and numbered pages. Such records will be dated and signed or otherwise authenticated on the day of entry.
- Records retained on file shall be indexed. The indexing system shall include as a minimum the location of records within the indexing system (which shall be in alphabetical, chronological, or numerical order.
- There shall be sufficient information in records to permit identification between the record and the item(s) or activity to which it applies. Identification of records will be by means that permit traceability.
- The records storage system shall provide for accurate retrieval of records without undue delay.
A number of QA/QC samples will be collected to check the adequacy of sample collection and analysis and to monitor laboratory performance.

Duplicates, blanks, and spiked samples are used to test the sampling technique to determine if the technique affects the analytical results, to measure the internal consistency of the samples, and to estimate any variance or bias in the analytical process. The field and laboratory QA/QC sampling procedures are described below.

10.1 FIELD SAMPLING QC PROCEDURES

QC replicate (duplicate) samples and blanks are used to provide a measure of the internal consistency of the samples and an estimate of variance and bias. Table 4-2 shows the collection frequencies of the field QC samples.

Blanks provide a measure of cross-contamination sources, decontamination efficiency, and other potential errors that can be introduced from sources other than the sample.

One field blank will be included with each daily shipment of groundwater samples. The field blanks will indicate if any contamination has been caused by the sampler or by handling the sample bottle in the field. The sample container will be filled with distilled, deionized water in the field at the time of sampling. Preservatives will be added as appropriate and the sample container capped, packed, and shipped with the samples.

A field replicate (duplicate) will be collected at a frequency of one per 10 samples or at a minimum of one per sampling event if sample volume is available. Since CH2M HILL is already obtaining split samples for the fish, mussels, and macroinvertebrates, there may not be enough volume to divide the split sample further to obtain the duplicate sample.

10.2 LABORATORY ANALYTICAL QC PROCEDURES

The analytical laboratory will use all of the QC elements of the EPA CLP and the corresponding current inorganic SOW. NBS or NRC reference materials will be analyzed where appropriate in lieu of MSs (See Table 4-2).
Matrix Spike

The MS for total mercury will be spiked in a separate aliquot of a sample selected from a batch of 10 field samples as specified in Table 4-2. The MS will be used to assess accuracy.

Laboratory Blanks

Method blanks will be analyzed for background contamination from the laboratory as specified in the analytical SOW (Appendices A and D).

WDCR436/019.51
Audits of laboratories and field and testing activities will be conducted as a minimum once during activities that may affect the integrity of the sample program. The audits will cover, in general, verification that the following has occurred: 1) approved procedures are in place and being used, 2) an acceptable calibration program is in place, 3) an organization structure is in place and personnel responsibilities are clearly defined, 4) a training program for personnel is in place and current, 5) a COC program and a records retention program are in place, and 6) corrective action of variances by laboratory and field personnel is responsive and timely.

**LABORATORY PERFORMANCE AND SYSTEMS AUDITS**

The analytical laboratory will conduct both internal and external QC checks. External QC checks include participation in certification programs with EPA by analyzing QC samples of known concentrations received from EPA. Internal QC checks (replicates, spikes, and duplicates) are performed in accordance with CLP methods.

**FIELD TEAM PERFORMANCE AND SYSTEMS AUDITS**

A performance audit will be conducted by the SM and FC during the first week of sampling to verify that proper procedures are followed and that subsequent sample data will be valid. The audit will focus on the details of the QA program. The audit checklist, which will serve as the guide for the performance audit for field procedures, is shown in Figure 11-1. The audit will evaluate the organization of responsibilities to determine whether the QA organization is operational, as well as verify whether or not the following is taking place:

- Written procedures that are available are followed for collection of samples
- COC procedures are followed for traceability of sample origin
- The operational procedures are implemented so that the appropriate QC checks are being made in the field, and records are maintained of these checks
Figure 11-1  
FIELD PERFORMANCE AUDIT CHECKLIST

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<tr>
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<td>Date: ______________________</td>
</tr>
<tr>
<td>Project Location: ______________________</td>
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<tr>
<th>Yes __</th>
<th>No __</th>
<th>3) Are samples collected in the type of containers specified in the FSP?</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Comments: __________________________________________________________________</td>
<td></td>
</tr>
<tr>
<td></td>
<td>____________________________________________________________________________</td>
<td></td>
</tr>
</tbody>
</table>
Figure 11-1
(Continued)

Yes __ No __ 4) Is sample equipment available, calibrated, and in proper working order?
Comments ________________________________

Yes __ No __ 5) Are samples preserved as specified in the FSP?
Comments ________________________________

Yes __ No __ 6) Are the number, frequency, and type of samples collected as specified in the FSP?
Comments ________________________________

Yes __ No __ 7) Are QA checks performed as specified in the FSP?
Comments ________________________________

Yes __ No __ 8) Are photographs taken and documented as specified in the FSP?
Comments ________________________________

Document Control

Yes __ No __ 1) Have any accountable documents been lost?
Comments ________________________________

Yes __ No __ 2) Have any accountable documents been voided?
Comments ________________________________

Yes __ No __ 3) Have any accountable documents been disposed of?
Comments ________________________________
Figure 11-1
(Continued)

Yes __ No __ 4) Are the samples identified with sample tags?
Comments

Yes __ No __ 5) Are blank and duplicate samples properly identified?
Comments

Yes __ No __ 6) Are samples listed on a COC record?
Comments

Yes __ No __ 7) Is COC documented and maintained?
Comments

WDR436/021
Specified equipment is available, calibrated, and in proper working order
Sampling crews are adequately trained
Recordkeeping procedures are being followed; field notebooks, logsheets, bench sheets, and tracking forms are properly prepared and maintained
Corrective action procedures are followed

An audit report summarizing any results and corrections will be prepared and filed in the project files. Significant variances from established procedures will be reported to the RPM.
Section 12
PREVENTIVE MAINTENANCE

Routine maintenance procedures and schedules for sampling equipment are described in the manufacturers' instruction manuals. All records of inspection and maintenance will be dated and documented in the field notebook.

Maintenance procedures and schedules for all field and laboratory analytical instruments will be in strict accordance with the recommendations of the equipment manufacturers. Routine maintenance will be performed by laboratory personnel as needed. All records of inspection and maintenance will be dated and documented in laboratory record books.

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The precision and accuracy of data will be routinely assessed to ensure that they meet the requirements of the DQOs presented in Table 4-1. If enough data are generated, the precision, accuracy, and completeness may be assessed using statistical procedures.

Precision is commonly determined from duplicate samples; thus precision is usually expressed as RPD or relative standard deviation (RSD). These quantities are defined as follows.

\[
\text{RPD} = 100 \times \frac{2 \left| X_1 - X_2 \right|}{(X_1 + X_2)^2}
\]

\[
\text{RSD} = \left( \frac{100}{2} \right) \times \left[ \frac{2 \left| X_1 - X_2 \right|}{(X_1 + X_2)} \right]
\]

where \( X_1 \) and \( X_2 \) are the reported concentrations for each duplicate sample.

Accuracy is commonly presented as percent bias or percent recovery. Percent bias is a standardized average error; that is, the average error divided by the actual or spiked concentration and converted to a percentage. Percent bias is unitless so it allows the accuracy of analytical procedures to be compared easily.

Percent recovery provides the same information as percent bias. Accuracy is often determined from spiked samples. Percent recovery is defined as:

\[
\text{% Recovery} = \frac{R}{S} \times 100
\]

where \( S \) = spiked concentration
\( R \) = reported concentration

Given this definition it can be shown that

\[
\text{% bias} = \text{% recovery} - 100
\]
Section 14
CORRECTIVE ACTIONS

The SM is responsible for initiating corrective actions (CAs). CA steps will include problem identification, investigation responsibility assignment, investigation, action to eliminate the problem, increased monitoring of the effectiveness of the CA, and verification that the problem has been eliminated.

Documentation of the problem is important to the overall management of the study. A CA Request Form for problems associated with sample collection, shown in Table 14-1, will be completed by the person discovering the QA problem. This form identifies the problem, establishes possible causes, and designates the person responsible for action. The responsible person will be either the FM or the RTL.

The CA Request Form includes a description of the planned CA and has space for follow-up. The RTL will verify that initial action has been taken and appears to be effective and, at an appropriate later date, check again to ensure that the problem has been fully resolved. The RTL receives a copy of all CA Request Forms and enters them into the CA Log. This permanent record will aid the RTL in follow-up and will assist in resolving QA problems with the SM.

Examples of CAs include, but are not limited to, correcting COC forms, analysis reruns (if holding-time criteria permit), recalibration with fresh standards, replacement of sources of blank contamination, examination of calculation procedures, additional training in sample preparation and analysis, reassignment of analytical responsibilities using a different batch of containers, or recommending an audit of laboratory procedures. Additional approaches may include:

- Resampling and analyzing
- Evaluating and amending sampling and analytical procedures
- Accepting the data and acknowledging the level of uncertainty or inaccuracy by flagging the data and providing an explanation for the qualification
Table 14-1
CORRECTIVE ACTION REQUEST FORM  
(Sample Collection)

| Originator: _________________________ Date _________________________ |
| Person responsible for replying: ______________________________________ |
| Description of problem and when identified: ____________________________ |
| State cause of problem, if known or suspected: ________________________ |
| Sequence of Corrective Action (CA): (If no responsible person is identified, submit this form directly to the RTL.) |
| State date, person, and action planned: ________________________________ |
| CA initially approved by: _________________________ Date: ______________ |
| Follow-up date: ____________________________________ |
| Final CA approval by: _________________________ Date: ______________ |
| Information copies to: ____________________________________________ |
| RESPONSIBLE PERSON: _____________________________________________ |
| RTL: ________________________________________________________ |
| SM: __________________________________________________________ |

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Section 15
QUALITY ASSURANCE REPORTS

A QA report will be completed at the end of the field activity to summarize the QA/QC status of the project and any problems. The report will be an assessment of the measured QA parameters (e.g., precision, accuracy); results of performance audits; any reported non-conformance; and any significant QA problems and the recommended solutions. Any change in the QAPjP will be summarized in a report or letter and sent to the RPM and distributed to the CH2M HILL project team.

For this project, no separate report is anticipated to describe the QA/QC achieved. The final project report will contain separate QA sections that summarize QA/QC information generated during the course of the project.

WDGR436/026.50
APPENDIX A

STATEMENT OF WORK
ANALYSIS OF VARIOUS MEDIA
FOR
METHYLMERCURY AND TOTAL MERCURY
STATEMENT OF WORK
ANALYSIS OF VARIOUS MEDIA FOR METHYLMERCUry AND TOTAL MERCURY

1.0 OVERVIEW OF PROJECT

1.1 INTRODUCTION

This Statement of Work (SOW) delineates the subcontract laboratory requirements for the analysis of various media for methylmercury and total mercury. Samples of fish, soil, waste, macroinvertebrates, and mussels will be collected at the Saltville site and analyzed for total mercury using SW-846, Method 7471 (with digestion step modifications); these samples will also be analyzed for methylmercury using a method developed by Bloom.\(^1\) Samples of groundwater will also be collected at the site and analyzed for total mercury using SW-846, Method 7470.

The subcontract laboratory must use safe handling procedures and generally accepted good laboratory practices in preparing and analyzing the above mentioned samples for methylmercury and total mercury.

1.2 GENERAL DESCRIPTION OF ANALYTICAL SERVICES

Samples from the various media will be analyzed for methylmercury and total mercury. To accomplish this task, the following requirements must be met:

- The analytical procedures as specified in Exhibits A, B, and C must be followed without deviation.
- The laboratory quality assurance (QA) and quality control (QC) requirements contained in Exhibits A, B, and C must be followed.
- Sample re-analysis requirements for total mercury will be consistent with those outlined by the CLP SOW for Inorganics (7/88).
- Strict chain-of-custody must be maintained for all samples, from the time of collection to the completion of all analyses.

2.0 SUMMARY OF REQUIREMENTS

The laboratory must perform all analyses and related activities in accordance with this SOW. The main body of the SOW describes the general requirements of the analysis of the various media for methylmercury and total mercury while specific details are further described in the Exhibits A through C. Requests for clarifications on requirements or perceived conflicts in requirements between the main body and Exhibits A through C must be communicated in writing at the earliest possible time to CH2M HILL's Site Manager for appropriate action or resolution.

2.1 QUALIFICATIONS AND EXPERIENCE

The laboratory must provide appropriate equipment and experienced personnel to measure methylmercury and total mercury in various media. The laboratory must designate and use experienced personnel who must meet the minimum requirements specified below and comply with all terms and conditions of the SOW. The EPA and CH2M HILL reserve the right to review personnel qualifications and reject those not meeting the minimum experience requirements. Experience is defined as at least 50 percent of an individual's productive work time spent in active participation on a given task or equivalent experience as approved by CH2M HILL's Site Manager.

The goal is to use the most experienced personnel available.

- The operator using the Bloom method of determining methylmercury in various media by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection, must have at least 6 months of experience with this method.

- The operator using SW-846, Method 7470 or 7471, for the determination of total mercury in various media, must have at least 3 months of experience with these methods.

- The laboratory supervisor or data interpretation analyst working on the project must have at least 6 months experience in the operation of the Bloom method.

2.2 QUALITY ASSURANCE PLAN

The laboratory must provide an acceptable QA plan to CH2M HILL and have it available for inspection during any EPA onsite audits. The QA plan must include standard operating
procedures (SOP) for the analysis of methylmercury and total mercury in various media. The QA plan and related documents (i.e., SOPs) must include, but not be limited to:

- Project organization and responsibility. Designation of all laboratory operation and QA personnel and definition of their responsibilities. Resumes of all project personnel must be attached detailing applicable experience. All personnel must meet the minimum requirements outlined in Section 2.1 above.

- General description of laboratory facilities and identification of specific major equipment dedicated to this project. Include backups available should the primary equipment become unusable.

- Description of laboratory chain-of-custody procedures.

- Description of laboratory data reduction, review and reporting procedures.

- Description of internal laboratory QC procedures.

- Description of corrective action procedures for out-of-control conditions.

- Description of preventive maintenance procedures.

2.3 CHAIN-OF-CUSTODY AND DOCUMENTATION CONTROL

The laboratory must have chain-of-custody procedures that are consistent with chain-of-custody elements outlined in the CLP SOW (7/88). Documentation is required to show that all procedures are being strictly followed. This documentation must be maintained as a specific case file designed for this study.

2.4 LABORATORY QA/QC REQUIREMENTS

The laboratory is responsible for implementing and performing QC procedures specified below at the required frequencies described. EPA and CH2M HILL reserve the right to review the frequency and results of QC analyses and to reject those not meeting the minimum requirements. For sample reanalysis caused by contractor deficiencies, the sample analysis is not accountable and billable. The following summarizes the QA/QC requirements:

- Laboratory must successfully analyze (i.e., results are within the range given by NBS) a performance evaluation sample (PE-NBS) for methylmercury.
The laboratory must analyze a PE-NBS sample at a frequency of 1 per 20 or fewer field samples in lieu of a matrix spike sample for methylmercury.

The laboratory must follow the QC requirements as specified in SW-846, Methods 7470 and 7471, for total mercury in various media (See Exhibits A and B).

2.5 SAMPLE REANALYSIS REQUIREMENTS

Certain samples may require sample reruns either because of problems with the sample matrix or laboratory deficiencies. Sample reanalysis necessitated by sample matrix problems or problems caused by CH2M HILL will be paid for; sample reanalysis due to laboratory deficiencies will not be paid for. Reanalysis samples are considered as additional field samples. Therefore, each reanalysis counts as one field sample in determining the QA/QC requirements as described above.

2.6 REPORTING REQUIREMENTS

The laboratory must follow package format of CLP Statement of Work for Inorganic Analysis (7/88) including all analyst logbook pages, run logs, raw data, calculations, data summary sheets, chain-of-custody (including laboratory chronicle forms that document sample custody within the laboratory), dates of sample analyses, and airbills. All report forms and data must be labeled with EPA sample number as per chain-of-custody and CLP forms. Results are to be reported in $\mu$g Hg/g. Records of analysis and calculations must be legible and sufficient to recalculate all concentrations. EPA or NBS QC reference sample, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95 percent confidence limits for analysis results will be provided for all reference samples used. All possible efforts should be made to minimize the holding/analysis/reporting times.

2.7 STANDARD OPERATING PROCEDURES

The laboratory must submit written SOPs in the following areas: chain-of-custody, sample receipt and log-in, sample storage and security, sample tracking, case file organization and assembly, analytical method (Exhibit A with laboratory-specific details), data reduction and validation, glassware cleaning, laboratory safety, instrument preventive maintenance, and corrective action. The SOPs must also be available for inspection during an onsite audit of PE sample analysis and continuing laboratory onsite audits. Failure of the laboratory to have written SOPs at the time specified may result in rejection of the contract.
2.8 ONSITE QA EVALUATION REQUIREMENTS

During the contract period of performance, EPA and/or its authorized representatives and CH2M HILL or its representatives will examine the subcontract laboratory's operation, in order to determine the extent to which the laboratory is maintaining its ability to meet the terms and conditions of this SOW. These QA evaluations may not be scheduled in advance, so that EPA/CH2M HILL examiners can observe how project work is normally performed. Similarly, these investigations may take place during any work shift at the laboratory.

2.9 STORAGE REQUIREMENTS

For purposes of review and further investigation, sample extracts and samples must be stored in a secure area for at least 1 year after the date of final data submission unless otherwise specifically requested in writing by CH2M HILL's Site Manager.

2.10 SUBCONTRACTING

Subcontracting of any portion of this SOW is not allowed and analysis may not be performed at any other facility/location of the corporation except the facility/location designated in the Subcontract Agreement. The laboratory must be capable of performing all work associated with extraction and analysis of the samples as stated in this SOW.

2.11 ACCEPTANCE PERFORMANCE REQUIREMENTS

During the SOW period of performance, the laboratory is required to provide QA/QC data to CH2M HILL upon request. Laboratories with data deliverables from QA/QC analyses, which are determined by the EPA/CH2M HILL to be acceptable in full accordance with QA/QC requirements and schedule, will be eligible for continuing sample analyses. If the QA/QC data deliverables do not meet the SOW requirements and still do not meet the SOW requirements after appropriate corrective actions have been taken, then EPA/CH2M HILL reserve the right to stop sample shipment to the laboratory.

If examination of the final data package for a particular sample or group of samples reveals QA/QC deficiencies that render the data unusable and the deficiencies cannot be corrected, no payment shall be made for the affected samples.
EXHIBIT A

SW-846, Method 7470—Total Mercury in Groundwater.
1. General description of analytical service requested:
   Analysis of groundwater for total mercury using SW-846, Method 7470 (attached).

2. Definition and number of work units involved: Approximately forty-eight (48) groundwater samples for total mercury using SW-846, Method 7470 (attached). All samples will be low level concentration. Unit count includes required duplicates and spike duplicates. Unit count does not include calibration standards or laboratory method blanks.

3. Estimated date(s) of collection: Groundwater samples will be collected quarterly starting approximately November 30, 1989 (approximately 12 samples per event).

4. Approximate number of days results required after lab receipt of samples: Samples must be analyzed within 14 days of VTSR. Completed data package required by 30 days of receipt of last sample.

5. Analytical protocol required: Analyze all samples using SW-846, Method 7470. The method is attached. The quantitation limit of the method is 0.20 ug Hg/L. Analyze one duplicate sample for every 10 samples. Analyze one matrix spike sample for every 10 samples (or per batch if fewer than 10 samples total). Verify calibration with an independently prepared check standard every 15 samples. Prepare calibration curves as given in Method 7470.

6. Analytical results required: Follow data package format of CLP, Statement of Work for Inorganic Analysis (revision of 7/88). Include all analyst logbook pages, run logs, raw data, calculations, data summary sheets, chain-of-custody (including laboratory chronicle forms that document sample custody within the laboratory), dates of sample analyses, copies of SAS packing lists, and airbills. Individual pages of the data packages must be numbered. All report forms and data must be labeled with EPA sample number as per chain-of-custody and CLP forms. Results are to be reported in ug Hg/L. Records of analysis and calculations must be legible and sufficient to recalculate all concentrations. EPA or NBS QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95 percent confidence limits for analysis results will be provided for all reference samples used.
7. **Data Requirements:**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Detection Limit</th>
<th>Precision Desired (+/- % or conc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mercury</td>
<td>0.20 ug Hg/l</td>
<td>+/- 20%</td>
</tr>
</tbody>
</table>

8. **Quality Control Requirements:** All QA/QC requirements shall be performed and reported as specified in CLP SOW for Inorganics Analysis (7/88). Follow procedures for quality control as given in Method 7470. Duplicates and matrix spikes should be analyzed as stated in the Analytical Protocol Required.

WDCR457/020.51
METHOD 7470

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.
3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

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Figure 1. Apparatus for flameless mercury determination.
4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M KMnO₄ and 10% H₂SO₄; or
2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid (H₂SO₄), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO₃), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H₂SO₄. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of Type II water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of Type II water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of Type II water. Add 10 mL of concentrated HNO₃ and adjust the volume to 100.0 mL (1 mL = 1 mg Hg).

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 g per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.
6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH < 2 with HNO₃. The suggested maximum holding times for these samples are 38 days in glass containers and 13 days in plastic containers.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing < 1.0 g of mercury, to a 300-mL BOD bottle. Add 5 mL of H₂SO₄ and 2.5 mL of concentrated HNO₃, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 µg of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H₂SO₄ and 2.5 mL of concentrated HNO₃ to each bottle. Add 15 mL of KMnO₄ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and

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continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.
9.0 Method Performance

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 References

EXHIBIT B

SW-846, Method 7471—Total Mercury in Soil/Waste, Fish, Mussels, and Macroinvertebrates.
EXHIBIT B

1. General description of analytical service requested:
Analysis of fish, soil, waste, macroinvertebrates, and mussels for total mercury using SW-846, Method 7471 with a perchloric acid digestion as per Feldman (attached).

2. Definition and number of work units involved: Approximately one hundred-forty (140) samples for total mercury using SW-846, Method 7471 with a perchloric acid digestion (attached). All samples will be low level concentration. Unit count includes required duplicates and spike samples. Unit count does not include calibration standards or laboratory method blanks. Samples will be sent to the laboratory homogenized and frozen.

3. Estimated date(s) of collection: Soil, waste, macroinvertebrates, and mussels (approximately 46 total) will be collected during one sampling event starting approximately November 30, 1989. Fish samples will be collected during two events, the first starting November 30, 1989, and the second starting in May, 1990 (approximately 47 samples per event).

4. Approximate number of days results required after lab receipt of samples: Samples must be analyzed within 14 days of VTSR. Completed data package required by 30 days of receipt of last sample.

5. Analytical protocol required: Analyze all samples using SW-846, Method 7471 with a perchloric acid digestion. The method is attached. The quantitation limit of the method is 0.1 ug Hg/g. Analyze one duplicate sample for every 10 samples. Analyze one matrix spike sample for every 10 samples (or per batch per matrix if fewer than 10 samples total) per matrix (i.e., soil, waste, fish, macroinvertebrates, and mussels). Verify calibration with an independently prepared check standard every 15 samples. Prepare calibration curves as given in Method 7471. Samples will be frozen; all liquids from sample container should be included in the analysis of the sample.

6. Analytical results required: Follow data package format of CLP, Statement of Work for Inorganic Analysis (revision of 7/88). Include all analyst logbook pages, run logs, raw data, calculations, data summary sheets, chain-of-custody (including laboratory chronicle forms that document sample custody within the laboratory), dates of sample analyses, copies of SAS packing lists, and airbills. Individual pages of the data packages must be numbered. All report forms and data must be labeled with EPA sample number as per chain-of-custody and CLP forms. Results are to be reported in ug Hg/g.
Records of analysis and calculations must be legible and sufficient to recalculate all concentrations. EPA or NBS QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.

7. Data Requirements:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Detection Limit</th>
<th>Precision Desired (+/- % or conc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total mercury</td>
<td>0.1 ug Hg/g</td>
<td>+/- 20%</td>
</tr>
</tbody>
</table>

8. Quality Control Requirements: All QA/QC requirements shall be performed and reported as specified in CLP SOW for Inorganics Analysis (7/88). Follow procedures for quality control as given in Method 7471. Duplicates and matrix spikes should be analyzed as stated in the Analytical Protocol Required.

WDOR457/021.51
1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.
4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature inside the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the
Figure 1. Apparatus for flameless mercury determination.
system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M KMnO₄ and 10% H₂SO₄, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO₃.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of Type II water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of Type II water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.
6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with nitric acid.

6.4 For solids or semisolids, moisture may be driven off in a drying oven at a temperature of 60°C.

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of Type II water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL Type II water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. CAUTION: Do this addition under a hood, as Cl₂ could be evolved. Add 55 mL of Type II water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H₂SO₄ and 2 mL of concentrated HNO₃ are added to the 0.2 g of sample. Add 5 mL of saturated KMnO₄ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with Type II water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 µg of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL Type II water and 15 mL of KMnO₄ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of Type II water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

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AR300702
7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.6 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.
9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES


<table>
<thead>
<tr>
<th>Sample Matrix</th>
<th>Preparation Method</th>
<th>Laboratory Replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission control dust</td>
<td>Not known</td>
<td>12, 12 ug/g</td>
</tr>
<tr>
<td>Wastewater treatment sludge</td>
<td>Not known</td>
<td>0.4, 0.28 ug/g</td>
</tr>
</tbody>
</table>
METHOD 7471

HgRCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

7.1 For sample preparation weigh 3 portions of dry sample; add Type II water and aqua regia to each

7.1 Heat; cool; add Type II water and potassium permanganate solution

7.1 Heat; cool; add sodium chloride, hydroxylamine sulfate and Type II water

7.1 Add stannous sulfate to each bottle; attach to aeration apparatus

7.2 Add conc. H_2SO_4 and conc. HNO_3 to sample; add KMnO_4 solution

7.2 Autoclave samples; cool; dilute; add sodium chloride hydroxylamine

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AR300706
Transfer aliquots of mercury working standard to series of bottles for standard preparation.

Add Type II water and aqueous regia to each bottle: heat.

Cool: add Type II water and KMnO₄ solution: heat; cool; add sodium chloride and hydroxylamine sulfate solution.

Add Type II water and stannous sulfate: attach to aeration apparatus.

For analysis, run circulating pump continuously, aerate.

Construct calibration curve: determine peak height and mercury value.

Analyze by method of standard additions.

Routinely analyze duplicates, spiked samples, and check standards.

Calculate metal concentrations.

Stop.
Table III. Characteristics of the Complexes

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Co(II) complex</th>
<th>Cu(II) complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Brown</td>
<td>Wine-red</td>
</tr>
<tr>
<td>λ_{max}</td>
<td>470 nm</td>
<td>450-520 nm</td>
</tr>
<tr>
<td>Beer's law range</td>
<td>0.20 μg/ml</td>
<td>0.6 μg/ml</td>
</tr>
<tr>
<td>Accurate range of determi-</td>
<td>0.5-19.6 μg/ml</td>
<td>0.6-5.8 μg/ml</td>
</tr>
<tr>
<td>Sandell's sensitivity (4)</td>
<td>0.015 μg/cm²</td>
<td>0.013 μg/cm²</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.002</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Cobalt Complex. The cobalt complex exhibits a broad maximum at 450-520 nm. The composition of the complex could not be accurately deduced by the application of the method of continuous variations. The limb on the excess-ligand side of the Job's curve did not show significant decrease in absorbance after 1:3 (cobalt:ferrozine) composition was attained in the solution. However, it seems that the species contains cobalt and the ligand in 1:3 ratio. The characteristics of the complex are summarized in Table III.

Interferences. In the determination of cobalt, at least to 1000 times the molar excess of each of fluoride, chloride, bromide, iodide, nitrite, nitrate, thiocyanate, chloride, acetate, sulfate, sulfite, borate, oxalate, citrate, phthalate, thiourea, and phosphate; 300 times without 100 times of each of alkaline earth metals, zinc, cadmium, mercury, tin, lead, bismuth, and manganese did not interfere. However, the presence of copper, iron, and nickel caused interference.

Simultaneous Determination. The magenta-colored ferric complex of ferrozine absorbs maximum at 562 nm with molar absorptivity 27,000 (1). On the other hand, λ_{max} of the cuprous complex lies at a much lower wavelength (470 nm). The two components were determined using the principle of additive absorptances and simultaneously solving Equations 1 and 2.

K_{470}Cu^{2+}Cu + K_{470}^{2+}Cu = F_1

(K_{total} absorbance at 470 nm)

K_{562}Cu^{2+}Cu + K_{562}^{2+}Cu = F_2

(K_{total} absorbance at 562 nm)

where K_{470}Cu, K_{562}Cu, K_{470}^{2+}Cu, and K_{562}^{2+}Cu, the molar absorptivities of copper and iron complexes at the given wavelengths are 4320, 3300, 9700, and 27900, l. mole cm⁻¹, respectively.

Received for review July 16, 1973. Accepted March 20, 1974. Financial assistance from the University Grants Commission under the program “Water Pollution” gratefully acknowledged.

**Perchloric Acid Procedure for Wet-Ashing Organics for the Determination of Mercury (and Other Metals)**

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To be useful for the determination of mercury, a wet-ashing procedure must meet the following requirements: 1) It must prevent the loss of mercury (and/or other elements of interest). 2) It must involve minimum risk of contamination. 3) It must be applicable to large (≤5-gram) samples of a wide range of materials, including animal tissue (fatty and lean), vegetation, soils, and up to 2 grams of coal and petroleum products. 4) It must be rapid. 5) It must require the minimum amount and the simplest types of apparatus. 6) It must permit processing many samples simultaneously, with minimum attention. 7) It must be safe.

Experience and a survey of the literature indicated that the G. Frederick Smith HClO₄-HNO₃ procedure (1) came closest to meeting these requirements, but that the procedure would have to be modified in order to fully satisfy requirements 4, 5, 6, and 7 if used on samples of the size and nature specified.

The essential features of the present procedure are: careful control of refluxing and evaporation by the use of temperature programming and an insulated air condenser, rather than a Bethge still (1); the use of certain minimum amounts of reagents per gram of sample; and use of the same vessel for digestion and storage.

Three general types of behavior were observed in the wet-ashing of various samples, and three variants of the basic procedure were developed to accommodate these. The category of treatment for each new type of material was established by preliminary tests on small amounts of material.

**EXPERIMENTAL**

**Apparatus.** Equipment used includes 250-ml borosilicate glass volumetric flasks with wide, flat bottoms (e.g., Kimax); supplying underground glass joints, with jackets of woven asbestos tubing held in place by wrapping with Teflon sealing tape (See Figure 1); variable temperature hotplates with specific power of at least 1.7 watts/cm² (e.g., Thermolyne Model 9425 or Type 2200) and sufficient area for the work load expected; surface temperature thermometers (e.g., PTC Model 51 G, manufactured by Pacific Transducer Company, Los Angeles, Calif.).
When the flasks have cooled, seal their mouths with cellulose tape to prevent contamination during storage. If, after use, the upper surface of a flask appears to be coated with dehydrated silica, remove the coating by rinsing the flask with 2% HF solution. Rinse and rinse the supplemental air condensers before use.

Reagents. Analyze all available batches of reagent grade HCIO₄ and select the batch lowest in mercury and/or other contaminants of interest. If the samples to be analyzed are expected to be very dense, and dilute the solution to volume, say to destroy the most resistant species in the sample. As far as is known, more than one inch of foam would be produced in 5 min). Allow the assembly to cool, rinse the condenser walls into the watre is mild, carry out the first heating stage (hot plate temperature 200°). If the reaction at that stage (i.e., refluxing of HNO₃) appears to be too vigorous to permit scaling up to a larger sample, use the CNP procedure for this material instead. If the first stage reaction is smooth, proceed to the second stage (hot plate temperature 265°). If the foam produced by the test sample at the second stage indicates that more than one inch of foam would be produced by a full size sample, use the SNP procedure for this material instead. If the amount of foam produced is moderate, carry the CNP procedure to completion. In doubtful cases, process a second test sample of intermediate size (~0.5 gram) as above.

To expedite evaporation, it is convenient to maintain three separate hotplates at the same hot plate temperature indicated. Perform all addition and heating of acids in a hood which is equipped for handling HCIO₄ and HNO₃ fumes.

CNP Procedure. Transfer ~20 mg granular K₂Cr₂O₇ to a 250-ml volumetric flask. Deposit 5 grams of sample or less in the flask, say a glass rod, if necessary, to push the sample into the lower portion of the flask. Add 10-15 ml of concentrated HNO₃ and 15 ml of concentrated HClO₄. Swirl the flask gently and affix a supplemental air condenser to it (Figure 1). Place the assembly on the first hotplate (surface temperature 200° ± 5°C); allow it to remain there until evolution of NO₂ fumes has essentially ceased (20-30 min). The solution is usually tan or brown at this stage. Transfer the assembly to the second hotplate (surface temperature 265° ± 5°C) and allow it to remain there for approximately 30 min (during this period, the color of the solution gradually changes to emerald green, owing to the disappearance of organic substances masking the color of the Cr³⁺ ion.) Next transfer the assembly to the third hotplate (surface temperature 340° ± 5°C), and allow it to remain there until the color of the solution changes to bright orange (usually 45 min or less). Remove the assembly from the hotplate, and allow it to cool to approximately room temperature. Add the first portions of distilled water through the supplemental air condenser to rinse any condensate into the flask. Remove the supplemental condenser, and dilute the solution to volume.

DNP Procedure. Transfer the sample (2 grams or less) to a 250-ml volumetric flask, treat with 5 ml H₂O₂ and then with 15 ml of concentrated HNO₃. Affix the supplemental air condenser to the flask, seal the assembly, and allow it to stand until the initial reaction has subsided. Place the assembly on the 230° hotplate, and follow the CNP procedure from that point on.

SNP Procedure. Transfer the sample (5 grams or less) to a 250-ml volumetric flask. Add 15 ml concentrated H₂SO₄, affix the supplemental air condenser, swirl the assembly, and place it on the 205° hotplate for 15 min. Remove the assembly from the hotplate, allow assembly to cool to room temperature, and then cool the lower part under cold running water. Slowly, and with swirling, add 25 ml concentrated HNO₃ through the supplemental air condenser. Return the assembly to the 230° hotplate for 60 min. Add 20 ml concentrated HCIO₄, and place the assembly on the 205° hotplate for 30 min. Transfer the assembly to the 240° hotplate and allow it to remain until the solution turns orange (usually less than 45 min). Allow the assembly to cool, rinse the condenser walls into the flask, remove the supplemental condenser, and dilute solution to mark. Use caution in the rinsing and diluting, since the heat of mixing of water with the final H₂SO₄·HCIO₄ mixture is high.

RESULTS AND DISCUSSION

The usefulness of the present procedure is measured by the degree to which it satisfies the requirements stated in the introductory paragraph. All Hg analyses not otherwise described were performed by the cold vapor atomic absorption method.

Prevention of Loss of Mercury during Wet-Ashing. In the present procedure, oxidation of organic matter is followed by preferential distillation of various amounts of H₂O, HNO₃, HClO₄ and reaction products away from mercury compounds. It is a basic assumption of this approach that the dewlines of the volatile mercury species present are lower than those of the degradation by-products and hydrates of perchloric acid which are to be eliminated. Retention of the mercury during the elimination of the other components means that as the temperature of the solution rises, the dewline for condensation of mercury compounds must remain safely below the top of the condenser, while the dewlines of the compounds eliminated rise above it. For the solution to attain the high oxidation potentials necessary to destroy the most resistant species in the sample, the concentration of HClO₄ in the solution must be permitted to approach the water-HClO₄ azeotrope.

It must be kept in mind that the air condenser actually consists of two parts: the neck of the reaction flask and the supplemental condenser shown in Figure 1. Preliminary experiments showed that a bare glass supplemental condenser of the dimensions given in Figure 1 was satisfactory for retaining mercury compounds while eliminating water and some nitric acid and degradation products. However, this type of condenser caused total refluxing of perchloric acid at the temperatures which could safely be used, thus setting a limit to the solution oxidation potential which could be achieved by evaporation. Two methods were possible for promoting the elimination of HClO₄ with minimal increase.
in the volatility of Hg compounds: a) the air condenser might be shortened until its top was at the dewline of the solution which had the composition and oxidation potential desired. However, this operation would also bring the top of the condenser closer to the dewline of the mercury compounds, making their retention more difficult. b) The supplemental air condenser might be thermally insulated. This would elevate only those dewlines which previously had fallen within this portion of the condenser. Thermal insulation of the upper portion of the condensing system would warm this area, and elevate the dewlines of the hydrates of perchloric acid, thus promoting their elimination from the system. The mercury compounds, whose dewlines lie at lower levels, would be much less affected. It was therefore decided to insulate the supplemental air condensers.

The above picture of preferential distillation presupposes that the net loss of vapor from the system is slow enough and steady enough to permit the establishment of stable dewlines. Reactions which produce too much effervescence, or produce it too suddenly, may cause enough turbulence or bulk transport of vapors in the air condenser column to eliminate mercury compounds which would be retained under steadier conditions. For this reason alone—aside from safety considerations (see below)—the rate of boiling and/or effervescence should be kept at a moderate level.

The retention of mercury during the wet-ashing procedure was tested in two ways: by measuring the recovery of known amounts of mercury compounds added to the sample before wet-ashing, and by comparing the Hg concentration values obtained by other methods. As tests of the present procedure for losses of Hg during wet-ashing, recovery experiments have the advantage of dealing with an accurately known amount of a known compound. However, they cannot prove the absence of losses of Hg in the chemical form (usually unknown) in which it occurs in the sample. The latter can be best done by comparing the present results with results obtained on the same material by other

Table I. Recovery of Hg Added to Tissue Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hg added, as</th>
<th>Wet-ashing procedure</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ocean perch, 5 g</td>
<td>1.02 as (C11H22)</td>
<td>CNP</td>
<td>98.5</td>
</tr>
<tr>
<td>Ocean perch, 5 g</td>
<td>0.969 (as C11H11gC2H4O2)</td>
<td>CNP</td>
<td>102.0</td>
</tr>
<tr>
<td>Cigarette smoke condensate, 0.5 g</td>
<td>1.03 as C11H11gCl</td>
<td>DNP</td>
<td>98.0</td>
</tr>
<tr>
<td>Sausage meat, 0.00 (as Hg(NO3)2)</td>
<td>SNP</td>
<td>98.1</td>
<td></td>
</tr>
</tbody>
</table>

Table II. Comparison of Mercury Concentrations Found by Various Methods

<table>
<thead>
<tr>
<th>Material</th>
<th>ppm Hg found by Present method Isotope dilution</th>
<th>Neutron activation</th>
<th>NBS Certified Value</th>
<th>USBM &quot;Best Value&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBS SRM 1571 (orchard leaves)</td>
<td>0.146</td>
<td>0.45</td>
<td>0.155</td>
<td>0.016</td>
</tr>
<tr>
<td>NBS SRM 1577 (bovine liver)</td>
<td>0.020</td>
<td>1.80</td>
<td>0.016</td>
<td>0.110</td>
</tr>
<tr>
<td>Fresh frozen tuna muscle No. 12</td>
<td>0.425</td>
<td>1.06</td>
<td>0.12</td>
<td>0.08</td>
</tr>
<tr>
<td>Fresh frozen tuna muscle No. 16</td>
<td>1.80</td>
<td>0.135</td>
<td>0.210</td>
<td>0.24</td>
</tr>
<tr>
<td>Coal, Washington County, Pa.</td>
<td>0.255</td>
<td>0.279</td>
<td>0.041</td>
<td>0.85</td>
</tr>
<tr>
<td>Coal, Muhlenberg County, Ky.</td>
<td>0.198</td>
<td>0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal, Jefferson County, Ohio</td>
<td>0.135</td>
<td>0.210</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal, Monroese County, Tenn.</td>
<td>0.017</td>
<td>0.91</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The mean value of the ratio of the result obtained by the present method to that obtained by neutron activation: 1.02 ± 0.09; the corresponding ratio for the U.S. Bureau of Mines "Best Value" is 1.04 ± 0.05. Thus the results in Tables I and II, as a whole, indicate essentially quantitative retention of mercury in the present procedure.

**Contamination.** The principal sources of contamination are reagents, glassware, and atmospheric dust. Batches of reagent grade concentrated HClO4 examined so far contained 0.064-11.2 ng/ml Hg. Reagent grade concentrated HNO3 usually showed 0.1-0.2 ng/ml Hg; this was reduced to 0.02 ng/ml by distillation in quartz when necessary. Reagent grade concentrated H2SO4 contained 0.28 ng/ml Hg. Digestions of blank solutions in flasks which had been baked and sealed as described above gave totals of values differing by less than 2 ng from those obtained by analyzing the reagents without digestion. This implies contamination from glassware and atmospheric dust to be negligible.

**Versatility.** This procedure proved applicable to samples received for analysis over a period of two years. Most samples (e.g., muscle and other low-lipid tissues, soils) were oxidized smoothly by the CNP procedure. Some samples (e.g., light tars, wheat flour, redistilled ethyl alcohol) reacted vigorously with concentrated nitric acid; with these, it was necessary to use the DNP procedure. With high-lipid materials (e.g., fatty tissues, beet liver) it was usually advisable to use the SNP procedure.

**Time Required.** Depending on the size and composition of the sample, the total time required for digestion was 90-100 min for the CNP and DNP procedures and 140-150 min for the SNP method.

**Apparatus Required.** One 250-ml volumetric flask and one standard taper joint are required for each sample.

Sample Throughput; Monitoring. The number of samples which can be wet-ashed simultaneously depends primarily on the hot plate area available. The Thermolyne Model 3425 can accommodate five 250-ml volumetric flasks; the Thermolyne Model 2200 can accommodate ten. The operator's attention to the digestion process is required only for transferring flasks and for observing the color of the digestion. As the color of each solution on the hot plate turns from green to orange, the operator should remove the flask from the hot plate in order to minimize the risk of losing mercury.

Safety. An explosion may result if hot, concentrated \( \text{HClO}_4 \) is allowed to come into contact with easily oxidized substances. Analysts usually deal with this hazard by first treating the sample with concentrated \( \text{HNO}_3 \) or a mixture of \( \text{HNO}_3 \) and \( \text{HClO}_4 \). This treatment is adequate for samples containing lipids, provided that sufficient \( \text{HNO}_3 \) (e.g., 15 ml for 0-5 grams of wet tissue) is used, and provided that the \( \text{HNO}_3 \) remains in the system until all of the easily oxidizable material has been oxidized. This can be assured by total refluxing of the \( \text{HNO}_3 \); if a beaker and a smooth glass are used to wet-ash a large sample, much of the \( \text{NO}_x \) may escape at the pouring lip of the beaker before the easily oxidized material has been oxidized. If the temperature is then raised in the presence of \( \text{HClO}_4 \), an explosion may occur.

Acknowledgment

The author is grateful to J. F. Emery for performing the neutron activation analyses given in Table II, and to J. A. Carter for performing the mass spectrometric analyses quoted in the same table.

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1,2,3-Phenyloxyamidine—A New Type of Analytical Reagent

Solvent Extraction and Spectrophotometric Determination of Vanadium(V)

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Department of Chemistry, Ravishankar University, Raipur (M.P.), India

During the course of investigations on the development of new organic analytical reagents, we are able to introduce a new type of functional grouping, \( \text{I} \), for metal ions.

\[
\begin{align*}
\text{I} & = \text{N} \quad \text{OH} \\
   & = \quad \text{N} \\
\end{align*}
\]

\( \text{I} \), the parent compound, possesses several useful properties as an analytical reagent. It is stable and can be readily prepared from common laboratory chemicals. The new agent has great potentialities for the colorimetric and spectrophotometric determination of metal ions. Studies carried out in these laboratories showed that this is an excellent agent for the spectrophotometric determination of vanadium(V) by solvent extraction and for the gravimetric determination of copper(II) and nickel(II).

Compared to well known cupferron (1), \( N \)-henzoyal-\( N \)-phenylhydroxyamine (2-5), and 3-hydroxy-1,3-diphenyl triazine (6), the proposed reagent has a wider scope as an analytical reagent. By substitution in the phenyl group attached to the coordinating nitrogen, certain groups can be introduced into the molecule of this organic compound with a view to modifying its complexing properties.

A method is presented for the spectrophotometric determination of vanadium(V) using 1,2,3-phenyloxyami-
EXHIBIT C

EXHIBIT C

1. General description of analytical service requested:

2. Definition and number of work units involved: Approximately one hundred-forty (140) samples for methylmercury using a method developed by Bloom (attached). All samples will be low level concentration. NBS methyl mercury reference material will be analyzed instead of matrix spike samples. Unit count includes required duplicates and NBS methylmercury reference material. Unit count does not include calibration standards or laboratory method blanks. Samples will be sent to the laboratory homogenized and frozen.

3. Estimated date(s) of collection: Soil, waste, macroinvertebrates, and mussels (approximately 46 total) will be collected during one sampling event starting approximately November 30, 1989. Fish samples will be collected during two events, the first starting November 30, 1989, and the second starting in May, 1990 (approximately 47 samples per event).

4. Approximate number of days results required after lab receipt of samples: Samples must be analyzed within 14 days of VTSR. Completed data package required by 30 days of receipt of last sample.

5. Analytical protocol required: Analyze all samples using a method developed by Bloom. The method is attached. The quantitation limit of the method should be 0.25 μg Hg/g or lower. Analyze one duplicate sample for every 10 samples. Analyze one NBS methylmercury reference sample (replaces the analysis of matrix samples) for every 10 samples (or per batch per matrix if fewer than 10 samples total) per matrix (i.e., soil, waste, fish, macroinvertebrates, and mussels). Verify calibration with an independently prepared check standard every 15 samples. Samples will be frozen; all liquids from sample container should be included in the analysis of the sample.

6. Analytical results required: Information provided in the data packages should be consistent with that of the CLP. The following information should be provided for all samples, including QC samples and references samples. Include all analyst logbook pages, run logs, raw data including instrument input and written data, calibration data, calculations, data summary sheets, chain-of-custody (including laboratory chronicle forms
that document sample custody within the laboratory),
dates of sample analyses, copies of SAS packing lists,
and airbills. Individual pages of the data package
must be numbered. All report forms and data must be
labeled with EPA sample number as per chain-of-custody
and CLP forms. Results are to be reported in μg Hg/g.
Records of analysis and calculations must be legible
and sufficient to recalculate all concentrations. EPA
or NBS QC reference samples, or any other reference
sample or initial calibration verification, will be
identified as to source, lot number, and sample number.
Corresponding "true" or target values and associated
95% confidence limits for analysis results will be
provided for all reference samples used.

7. Data Requirements:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Detection Limit</th>
<th>Precision Desired (±% or conc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylmercury</td>
<td>0.25 μg Hg/g</td>
<td>+/- 20%</td>
</tr>
<tr>
<td></td>
<td>(or lower)</td>
<td></td>
</tr>
</tbody>
</table>

8. Quality Control Requirements: Duplicates and NBS
methylmercury reference standards should be analyzed as
stated in the Analytical Protocol Required.

WDCR457/101.51
A technique is presented, which allows the rapid and precise determination of methylmercury in aqueous samples. The sample is first reacted with sodium tetraethylborate, to convert the nonvolatile monomethyl mercury to gaseous methylethylmercury. The volatile adduct is then purged from solution, and recollected on a graphitic carbon column at room temperature. The methylethylmercury is then thermally desorbed from the column, and analyzed by cryogenic gas chromatography with cold vapour atomic fluorescence detection. The method allows the simultaneous determination of labile Hg(II) species, through the formation of diethylmercury, and of dimethylmercury, which is not ethylated. The methylmercury detection limit is about 0.6 pg Hg, or 0.003 ng L⁻¹ for a 200-mL sample. The technique has been successfully applied directly to a wide variety of freshwater samples and alkaline tissue digestates. Seawater is analyzed following a simple extraction step to separate the methylmercury from the interfering chloride matrix. Analyses of natural surface waters have shown methylmercury levels typically in the range of 0.02–0.10 ng L⁻¹, with values as high as 0.64 ng L⁻¹ in a polluted urban lake. Waters collected from the anoxic bottom waters of a stratified remote lake have shown methylmercury levels as high as 4 ng L⁻¹ as Hg.

Although many lines of evidence support the conclusion that methylmercury is cycling through the biosphere, and may be disproportionately important in the overall global mercury cycle (Ballantine and Zoller 1984; Craig and Morton 1983; Jemelov 1970; Topping and Davies 1981; Westoo 1967) no adequate method has yet been introduced for the rapid, precise, and accurate determination of this species in ambient aqueous media. Solvent extraction, followed by chromatography has long been applied to the determination of monomethylmercury in tissues and sediments, where the observed levels are in the parts-per-million range (Craig and Morton 1983; Westoo 1967; O’reilly 1982; Holak 1982). Attempts to directly apply these technologies to the analysis of very large water samples have proved to be cumbersome, and to provide barely adequate detection limits for the accurate study of the environmental methylmercury cycle. These methods employ a variety of means of extraction from a large volume of water, such as resins (Robertson et al. 1987), solvents (Chiba et al. 1983; Robertson et al. 1987; Paudyn and Van Loon 1986), or sulfated adsorbents (Lee 1987). When extracted onto a solid support, the methylmercury is then eluted and back-extracted into a solvent, prior to analysis by gas chromatography. Although each differs in detail, these methods all suffer from common drawbacks: (1) large samples are required, leading to cumbersome procedures and long processing time, (2) the overall extraction yield of the process is often uncomfortably low (50–80%), and (3) dimethylmercury, if it is present, is not detected as a separate species thus confusing our understanding of the methylmercury cycle.

In this paper, a novel method for the determination of methylmercury in water is presented, which successfully addresses the above drawbacks, while simultaneously providing a detection limit of 0.003 ng L⁻¹ for a 200-mL sample. This is sufficient to accurately measure methylmercury in most ambient
winters, including precipitation and remote lakes. The method reported applies an aqueous phase reaction which converts ionic mercury species to their volatile ethyl analogs (Rapsomanikis et al. 1985). In this process, aqueous tetraethylborate anion reacts with labile HgX species to form diethylmercury. Elemental mercury and dimethylmercury, being nonionic, do not react with the tetraethylborate anion, and so also may be specifically determined. The volatile species are purged from solution onto a graphitic carbon trap, and then analyzed using cryogenic gas chromatography with a highly sensitive cold vapour atomic fluorescence detector (Bloom and Fitzgerald 1988).

**Experimental Materials**

**Cold Vapour Atomic Fluorescence Detector**

The CVAFS (cold vapour atomic fluorescence detector), described in detail by Bloom and Fitzgerald (1988), is built from readily available components. The excitation source is a 4-W low-pressure mercury vapour lamp, emitting predominantly at 254 nm (Ultra-Violet products, UVG-11), and the detector is a UV-Visible general purpose photomultiplier (Oriel 77340) shielded from stray light with a 253.7-nm interference filter (Oriel 56400). Atomic fluorescence is monitored at 90° to the direction of the excitation beam, through a 10-mm square quartz fluorescence cell (NSG Precision Cells 501F).

**Cryogenic Gas Chromatograph**

The cryogenic GC (gas chromatograph) column is configured as a U-tube within a sealed glass sheath (Bloom and Fitzgerald 1988), which serves to moderate the rate of heat transfer when the column is warmed during elution. The column, 80 cm in total length, is constructed from 6.4 mm outside diameter × 4 mm inside diameter borosilicate glass chromatography tubing. The sheath, also of borosilicate glass, is 2.5 cm in diameter, and 30 cm long. Prior to packing, the completed column is acid-cleaned and then silanized to deactivate the interior surfaces. The column is packed with 45 cm of pre-conditioned 15% OV-3 on Chromasorb W-AW-DMCS, 60/80 mesh (Bloom and Fitzgerald 1988; Andraea et al. 1981), held in place with silanized glass-wool plugs. Organomercury species are collected on the column held at −196°C in liquid nitrogen, under a flow of high purity helium. For analysis, the column is placed in a cylindrical oven held at 180°C, and the outflowing (40 mL·min⁻¹) carrier gas passed sequentially through a 900°C thermal decomposition tube, and the CVAFS detector cell. The decomposition tube consists of an 8-inch length of 9.5 mm outside diameter × 6 mm inside diameter quartz tubing with the central 7.6 cm packed with quartz wool. The tube is electrically heated with a winding of 18 gauge nichrome resistance wire. Thermal decomposition is necessary to render all eluted species as Hg°, the only form detectable by CVAFS.

**Fittings and Tubing**

Connections between components and columns are made using 6.4 mm or 9.5 mm outside diameter Teflon FEP tubing, and Teflon friction-fit or threaded tubing connectors. Friction-fit sleeves are 3-cm sections cut from unshrunken 6.4 mm or 9.5 mm inside diameter Teflon TFE heat-shrinkable tubing (Cole-Parmer Inst. Co.). Connections between components requiring mobility are made with 3.2 mm outside diameter Teflon FEP tubing, because of its greater degree of flexibility. All Teflon components are cleaned in hot concentrated HNO₃ prior to use.

**Purge Vessel**

The purge vessel is constructed from a 250-mL standard taper 24/40 glass-stoppered Erlenmeyer flask, with a special 4-way valve sparging-tube cap-assembly (Laboratory Data Control 700542). This valve assembly allows the water sample to react initially with the ethylating reagent, without bubbling, then to be purged onto the trapping column, and finally to be bypassed, so that water vapour adsorbed onto the column may be evaporated by the direct flow of dry carrier gas.

**Carbotrap Columns**

Columns for the pretapping of purified organomercury species are constructed from 6.4 mm outside diameter × 4.0 inside diameter silanized borosilicate chromatography tubing. The columns are 15.2 cm long, and packed with 7.6 cm of 20/40 mesh Carbotrap (graphitized carbon black, Supelco 2-0827), held in place with silanized glass wool plugs (Bloom and Fitzgerald 1988).

**Gases**

Helium is laboratory grade (Airco), further purified to <1 ppm O₂ with a high-temperature gas purifier (Supelco 2-3802). The gas is then passed through a gold-coated sand trap (Fitzgerald and Gill 1979) to remove mercury prior to use. Nitrogen and air are laboratory grade, passed first through activated carbon, then through gold-coated sand prior to use.

**Water**

All rinsing of containers and aqueous dilutions are made with tap water that has been running for at least 1 h before use. This water is found to be extremely low, and constant, in total mercury (0.3 ng·L⁻¹), at least one order of magnitude lower than our best laboratory deionized water. No methylmercury has been detected in our laboratory tap water, which comes from an on-site deep well.

**Gas Phase Mercury Standards**

Mercury standards are taken by airtight gas syringe from the headspace over the volatile compound of interest (Bloom and Fitzgerald 1988; Dumarey et al. 1985). For Hg°, about 5 g of the pure liquid is placed in a 250-mL amber glass bottle fitted with a septum-cap. For dimethylmercury, a 14 mg·L⁻¹ solution is prepared in octanol, and 25 mL placed into the bottle. A 200 mg·L⁻¹ solution is used for diethylmercury, owing to its lower vapour pressure. The organomercurial standards are calibrated daily against Hg°, using the gold-column/CVAFS system (Fitzgerald and Gill 1979).

**Methylmercury Standard**

Excess of methylmercuric chloride (Alfa 37123) is equilibrated with GC grade isopropanol at 20°C, to form a saturated solution. A concentrated stock solution, prepared by 1:1000 v/v dilution of the above in isopropanol, has been found to contain 4.16 mg·L⁻¹ total mercury, and 4.02 mg·L⁻¹ nonvolatile organic mercury, all of which is assumed to be in the mon-
omethyl form. A working standard solution prepared by a nominal 1:800 v/v dilution of the above in isopropanol, has repeatedly been analyzed and found to contain 5.40 \( \mu \)g·L\(^{-1}\) Hg as CH\(_3\)HgCl. This solution has been found to maintain both its total mercury concentration, as well as its methylmercury concentration for over 12 mo when stored in an amber glass bottle with Teflon cap, at a temperature of 0–5°C.

Sodium Tetraethylborate Solution

An approximately 1% solution of sodium tetraethylborate (STREM 11-0575) is freshly prepared every 2–3 d. Since this reagent is extremely air sensitive, it is not weighed, but rather measured by volume. Approximately 0.5 g (c.a. 2 cm\(^3\)) of the solid are quickly removed from the bottle, and added to 50 mL of cold water in a small Teflon FEP bottle. This solution is stored in the refrigerator except during use.

Sodium Acetate Buffer

Two moles of reagent grade sodium acetate (272 g) and 2 mol of Ultrex glacial acetic acid (118 mL) are dissolved in tap water to give a final volume of 1 L. This solution is purified of trace mercury by the addition of 5 g of 1N HCl-rinsed sulfhydryl chelating resin (Sumitomo Q-10R) to the bottle, and periodic agitation over a span of several days. The solution is then filtered, and stored in a Teflon FEP bottle, at room temperature.

Potassium Hydroxide/Methanol

Reagent grade KOH pellets (250 g) are dissolved in high purity methanol, to a final volume of 1 L. The solution is stored in a Teflon FEP bottle at room temperature.

Other Reagents

All acids, bases, and sodium chloride are reagent grade. Methylene chloride, methanol, and isopropanol are all high purity GC grade. All are stored in acid-cleaned Teflon FEP bottles, or glass bottles with Teflon FEP caps.

Procedures

Methylmercury in Freshwater Samples

Illustrated in Fig. 1 is a schematic diagram of the major steps involved in the procedure outlined below. A 100- to 200-mL water sample is placed into a 250-mL purging flask. Acetate buffer (200 \( \mu \)L) is added, bringing the pH to 4.9 ± 0.1. Sodium tetraethylborate solution (50 \( \mu \)L) is added, the flask swirled to mix, and the 4-way valve-cap inserted. The mixture is allowed to react without purging for 20 min. and then is purged with \( \text{N}_2 \) or air at a flowrate of 250 mL·min\(^{-1}\) for 25 min. The purge gas outflow is passed through a Carbotrap column to collect the volatile organomercury compounds. After the sample is purged,

![Diagram](image-url)
the valve is switched to pass dry gas over the column for 7 min. to remove residual water condensation from the trap.

The Carbotrap column is then connected in-line with the GC column, which is held in liquid nitrogen. The Carbotrap column is placed so that the end facing the bubbler output is now toward the GC column input. This avoids passing the organomercurial species down the entire length of the heated Carbotrap column during desorption, thereby greatly minimizing on-column breakdown of diethylmercury to the monoethyl form (Bloom and Fitzgerald 1988). Helium is allowed to flow through the cool Carbotrap column for 3 min, at 90 mL·min⁻¹, and then the column is electrically heated with 22-ga nichrome resistance wire for 10 min at a temperature of 300°C, under continuous helium flow.

Once sample desorption is completed, the cooled Carbotrap column is removed from the system, and the thermal decomposition tube and recorder/integrator are turned on. The GC column is then removed from the liquid nitrogen, and placed into a cylindrical oven held at 180°C. The mercury species are eluted in order of increasing molecular weight with the following retention times Hg°, 4.17 ± 0.07 min; (CH₃)₂Hg, 6.23 ± 0.14 min; CH₂CH₂HgCH₃, 7.25 ± 0.09 min; and (CH₃)₂Hg, 8.38 ± 0.17 min (Fig. 2). Elemental mercury is present both as a residual from the heating of the columns, and as a potential breakdown product of the organomercurials, and hence should be minimal. Hg° present in the aqueous sample passes through the Carbotrap column during the purging/drying steps and may be collected on a back-up gold trap. Methylmercury is the ethyl derivative of monomethylmercury, and diethylmercury is the ethyl derivative of inorganic labile mercuric species. Dimethylmercury is purged and detected unchanged by this method.

Small samples, such as tissue digests, pore water, etc., may be analyzed by dilution with tap water, and analysis as above. A smaller (25 mL) bubbler is used in these cases, and the purge time reduced to 10 min.

Preextraction of Samples Containing Complexing Agents

Because high levels of chloride (>200 ppm) are observed to inhibit the ethylation process, methylmercury in seawater must first be extracted from the chloride-rich matrix, and then be returned to a freshwater matrix. This is done by extracting a 100-mL sample, acidified to a pH of 2–5, with 3 consecutive 10-mL portions of methylene chloride, using a Teflon FEP separatory funnel. The methylene chloride extracts are combined in a 125-mL Teflon bottle, and the surface rinsed with 5 mL of tap water, without shaking, to remove residual saltwater droplets on the solvent surface. The tap water rinse is removed by pipetting. About 70 mL of tap water is then added to the methylene chloride, and the bottle placed in a hot water bath at 60°C until all of the CH₂Cl₂ has boiled away. The water is then purged for 10 min at 250 mL·min⁻¹ with N₂ to remove residual solvent. The monomethylmercury is now transferred to the freshwater matrix, which is analyzed as before.

This procedure may also be used to extract the total methylmercury component from freshwater samples containing organic complexing agents, high transition metals concentrations, or particulate matter which inhibits the complete recovery of methylmercury by the direct ethylation procedure. In these cases, 5 mL of a solution containing 30% KCl and 2% HCl are added to 100 mL of the sample and allowed to equilibrate for 2–4 h. The sample is then extracted as above.

**Digestion Procedure for Soft Tissues**

Approximately 1.0 g of homogenized wet tissue, or 0.25 g of pulverized freeze-dried tissue is accurately weighed into a 22-mL Teflon vial (Savillex 0275), and 10.0 mL of 25% KOH/methanol solution are added. The vial is vigorously shaken and the tissue is allowed to digest at room temperature for 24–48 h, or is placed in an ultrasonic bath for 1 h. The digest is then diluted to 20.0 mL with methanol. To analyze, 50 μL of the extract are added to 100 mL of tap water, and neutralized with...
50 μL 2.0 M acetic acid. After the addition of 200 μL of acetate buffer, the sample is analyzed as for a freshwater sample.

Results and Discussion

Optimization of Ethylation Parameters

Rapsomanikis et al. (1985) in their study of lead ethylation judged the following parameters as most important to optimize: pH, purge time and flow, and amount of reagent. While these authors used simplex optimization as a guide, the present work was based upon the more traditional systematic approach, which results in a clearer understanding of the importance of each factor, once the data have been collected. After using trial and error to obtain initial parameters which gave a strong signal, one parameter was systematically varied while holding the others constant. When an optimum was found for that parameter, it was then held constant at that level while the other parameters were varied in their turn. Once all of the optima were located, the process of varying each parameter in its turn, while holding all others at their optima was repeated to generate the data illustrated in Fig. 3a–d. For all of these determinations, 100 mL of tap water, spiked to contain 0.54 ng/L Hg as monomethylmercury was used as the test solution.

As can be seen in Fig. 3a, the pH of ethylation was a critical parameter, showing a broad optimum in the range of 4–7, and tailing off dramatically at both extremes. The yield diminishes at low pH because of rapid destruction of the ethylating agent by H+, while at high pH, the loss in yield seems to be caused by inhibition of the ethylation reaction—perhaps due to the formation of unreactive multihydroxyl methylmercury anions. As a matter of convenience, a pH of 4.9 was chosen, as this may be obtained using a 1:1 acetic acid/sodium acetate buffer. Fig. 3b and 3c show that the ethylation reaction was both very rapid, and required little reagent. The amount of reagent chosen, 50 μL of a 1% solution (5 ppm concentration in the sample) was in excess of the minimum necessary, but not so high as to lead to interferences in the GC elution, as will be discussed below. A reaction time of 20 min, and purge time of 25 min.
TABLE 5. Recovery of mercury species spiked into 1.0-g aliquots of freshwater white sucker (Catostomus commersoni) tissue prior to KOH/methanol digestion and analysis by ethylation/GC.

<table>
<thead>
<tr>
<th>Replicate</th>
<th>CH₃Hg (as Hg, ng·g⁻¹, wet wt.)</th>
<th>Hg(II) (as Hg, ng·g⁻¹, wet wt.)</th>
<th>(CH₃)₂Hg (as Hg, ng·g⁻¹, wet wt.)</th>
<th>CH₃Hg (as Hg, ng·g⁻¹, wet wt.)</th>
<th>Hg(II) (as Hg, ng·g⁻¹, wet wt.)</th>
<th>(CH₃)₂Hg (as Hg, ng·g⁻¹, wet wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>250</td>
<td>&lt;4.5</td>
<td>&lt;2.2</td>
<td>359</td>
<td>205</td>
<td>303</td>
</tr>
<tr>
<td>2</td>
<td>257</td>
<td>&lt;4.5</td>
<td>&lt;2.2</td>
<td>495</td>
<td>247</td>
<td>301</td>
</tr>
<tr>
<td>3</td>
<td>241</td>
<td>&lt;4.5</td>
<td>&lt;2.2</td>
<td>371</td>
<td>209</td>
<td>321</td>
</tr>
<tr>
<td>4</td>
<td>232</td>
<td>&lt;4.5</td>
<td>&lt;2.2</td>
<td>453</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>216</td>
<td>&lt;4.5</td>
<td>&lt;2.2</td>
<td>449</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>245</td>
<td>&lt;4.5</td>
<td>&lt;2.4</td>
<td>336</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>X</td>
<td>240</td>
<td>&lt;4.5</td>
<td>&lt;2.4</td>
<td>410</td>
<td>220</td>
<td>308</td>
</tr>
<tr>
<td>σ</td>
<td>14</td>
<td>—</td>
<td>—</td>
<td>64</td>
<td>23</td>
<td>11</td>
</tr>
<tr>
<td>Spike (ng)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>401</td>
<td>260</td>
</tr>
<tr>
<td>% Recovery</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>102.4</td>
<td>84.6</td>
</tr>
</tbody>
</table>

TABLE 6. Methylmercury and total mercury contents of various freshwater and marine fish.

<table>
<thead>
<tr>
<th>Fish species</th>
<th>Replicates</th>
<th>Methylmercury (µg·g⁻¹ wet wt.)</th>
<th>Total mercury (µg·g⁻¹ wet wt.)</th>
<th>Methylmercury (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chinook salmon (Oncorhynchus tsawytscha)</td>
<td>5</td>
<td>0.0418 ± 0.0042</td>
<td>0.0430 ± 0.0031</td>
<td>97.2</td>
</tr>
<tr>
<td>Pacific halibut (Hippoglossus stenolepis)</td>
<td>4</td>
<td>0.0555 ± 0.0080</td>
<td>0.0653 ± 0.0018</td>
<td>85.0</td>
</tr>
<tr>
<td>Yellow perch (Perca flavescens)</td>
<td>3</td>
<td>0.526 ± 0.070</td>
<td>0.568 ± 0.026</td>
<td>92.3</td>
</tr>
<tr>
<td>White sucker (Catostomus commersoni)</td>
<td>3</td>
<td>0.249 ± 0.008</td>
<td>0.231 ± 0.015</td>
<td>107.8</td>
</tr>
<tr>
<td>Northern pike (Esox lucius)</td>
<td>3</td>
<td>1.762 ± 0.072</td>
<td>1.661 ± 0.043</td>
<td>106.1</td>
</tr>
</tbody>
</table>

TABLE 7. Observations of mercury speciation in unfiltered natural waters collected in 1988. No dimethylmercury was observed in any sample.

<table>
<thead>
<tr>
<th>Water type</th>
<th>Location</th>
<th>Date</th>
<th>Total</th>
<th>Labile</th>
<th>Monomethyl</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligotrophic (surface)</td>
<td>Lake Crescent, WA</td>
<td>3/16/88</td>
<td>0.163</td>
<td>0.170</td>
<td>&lt;0.004</td>
<td>3</td>
</tr>
<tr>
<td>Mesotrophic (surface)</td>
<td>Lake Union, WA</td>
<td>2/25/88</td>
<td>1.69</td>
<td>0.072</td>
<td>0.039</td>
<td>4</td>
</tr>
<tr>
<td>Eutrophic (surface)</td>
<td>Onadaga, NY</td>
<td>2/28/88</td>
<td>10.68</td>
<td>0.523</td>
<td>0.636</td>
<td>2</td>
</tr>
<tr>
<td>Seawater (surface)</td>
<td>Sequim Bay, WA</td>
<td>5/2/88</td>
<td>0.357</td>
<td>0.089</td>
<td>0.016</td>
<td>3</td>
</tr>
<tr>
<td>Artesian well</td>
<td>Sequim, WA</td>
<td>6/29/88</td>
<td>0.289</td>
<td>0.183</td>
<td>&lt;0.002</td>
<td>2</td>
</tr>
<tr>
<td>Stratified (surface)</td>
<td>Little Rock, WI</td>
<td>9/10/88</td>
<td>1.06</td>
<td>0.03</td>
<td>0.125</td>
<td>2</td>
</tr>
<tr>
<td>Stratified (bottom)</td>
<td>Little Rock, WI</td>
<td>9/10/88</td>
<td>10.58</td>
<td>1.58</td>
<td>3.96</td>
<td>2</td>
</tr>
</tbody>
</table>

Values obtained by direct ethylation of the organic-rich waters were 0.041 ng·L⁻¹ Hg (surface) and 1.21 ng·L⁻¹ Hg (depth).

7.4. This is in accord with the observations of others (Robertson et al. 1987), and makes it clear that a sample containing methylmercuric chloride must be acidic to allow quantitative extraction into an organic solvent. It is also clear that strong acidification is not necessary for good yield, the distribution coefficients in this case being almost identical between pH 2 and pH 5. Since dimethylmercury is converted to monomethylmercury in the extraction procedure, untreated samples must be separately purged onto Carbotrap for the determination of (CH₃)₂Hg in seawater.

For the extraction of seawater, the working conditions were chosen to be acidification to pH = 1.9 (1.0 mL 12.7 N HCl
per litre of sample), followed by three consecutive 10-mL extractions with CHCl3. Table 4 illustrates the results of this procedure on spiked unfiltered water taken by hand-dipping from Sequim Bay, WA. This water was found to contain 0.357 ng L⁻¹ total mercury, and 0.089 ng L⁻¹ “acid labile” mercury. The salinity was about 30%. The blanks were determined by again subjecting the previously extracted sample to exactly the same reagents and procedures. As can be seen, there was a small reagent blank of 0.042 ± 0.003 ng L⁻¹ Hg methylmercury associated with the procedure. The source of this contamination was traced to the methylene chloride. The contamination could be reduced significantly by preextracting the solvent with 1.0 N NaOH in deionized water. The seawater samples were spiked with 0.32 ng L⁻¹ methylmercury to give a more realistic test of the procedure at low concentrations. When the small (0.016 ng L⁻¹) level of methylmercury already present in the water was considered, the recovery of the spike was observed to be 93.4 ± 9.4%.

Fish Tissues

Methylmercury speciation was analyzed from spiked and unspiked frozen samples of white sucker (Catosomus commersoni) collected from a small midwestern lake (Table 5). The yields for both monomethylmercury and dimethylmercury on these samples were close to 100%, while that for Hg(II) was lower, about 85%. Dimethylmercury recoveries reported were assessed by separate analysis of a nonethylated aliquot of fish tissue digestate diluted in 100 mL of tap water. Results of recoveries from the ethylation procedure, using air purging to eliminate the triethylborane inhibition were similar, although the variability was a factor of five greater.

Since each spike was added to a separate sample, an assessment of species interconversion was possible. In no case was any spike observed to result in the recovery of any species other than that which was added. The low yield for Hg(II) resulted from the partial conversion of the ionic form to Hg⁰, which was not retained by the Carbotrap, but was collected on a back-up gold trap. The higher variability of the monomethylmercury yield was attributable to the difficulty in pipetting the small volumes of organic-based sample extract necessary to keep the system on scale.

The digestion procedure outlined was applied to several species of fresh and saltwater fish (Table 6). In addition to mercury speciation analysis, total Hg analysis by hot concentrated HNO₃ digestion, followed by SnCl₂ reduction and gold trapping was employed. These results indicated that almost all of the mercury observed in these tissues was in the form of monomethylmercury, with undetectable levels of either labile inorganic or dimethylmercury. The exception was halibut (Hippoglossus stenolepis) which was observed to contain only 86% of its total as monomethylmercury, the rest being labile Hg(II) species.

Analysis of Environmental Waters

Naturally occurring waters from a variety of sources were analyzed to assess the adequacy of the methods and detection limits for application in the field (Table 7). Most surface waters investigated were found to contain low levels of monomethylmercury, with the highest levels (0.64 ng L⁻¹) being observed in the surface waters of a mercury and organic waste polluted urban lake (Onadaga Lake, Syracuse, NY). Dramatic elevations of methylmercury concentrations in the anoxic bottom waters of a stratified seepage lake (Little Rock Lake, WI) were observed through the summer of 1989, indicating a sediment source for methylmercury to the water column of this lake. Some representative data from this system are presented in Table 7, although the complete data set will be the subject of a future publication. Precipitation samples have been found to contain significant levels of monomethylmercury often approaching 5% of the total mercury content of the sample (Bloom and Watras 1989).

Conclusions

These results are an important positive proof of the ubiquity of methylmercury cycling in the environment, and indicate that the methods described in this paper are adequate for detailed quantitative studies of these processes. Studies are under way to assess the role of the methylmercury cycle within the overall global mercury cycle. The results should help clarify the role played by acid rain in the enhancement of methylmercury bioaccumulation by freshwater fish.

Acknowledgements

The results presented in this paper were obtained during work funded by the Electric Power Institute, under contract No. 25120-11173, and by Tetra Tech (California) under contract No. 25120-05850. Special thanks to Allya A. Bloom for his efforts in catching many of the fish used for development of analytical methods.

References


APPENDIX B

GOLD FILM MERCURY VAPOR ANALYZER
CALIBRATION PROCEDURE
APPENDIX B
GOLD FILM MERCURY VAPOR ANALYZER
CALIBRATION PROCEDURE

A calibration check is recommended after 20 hours of use. The purpose of the calibration check is to verify the proper operation of the instrument. If, when verifying calibration, you achieve results within the expected range, you may assume that the instrument is maintaining its calibration. Since the response of the Gold Film Sensor to mercury is inherently stable, the calibration setting should not require adjustment more often than annually.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Lightly shake the calibration vessel.</td>
<td></td>
</tr>
<tr>
<td>2. Leave the calibration vessel at stable room temperature for at least 2 hours.</td>
<td>2. The preferred temperature range for calibration check is 18-22°C. Avoid temperature fluctuations &gt;1°C per hour.</td>
</tr>
<tr>
<td>3. Unplug line cord and battery charger.</td>
<td></td>
</tr>
<tr>
<td>4. Change intake filter disc and septum.</td>
<td>4. See Pages B-2 and B-3. Always change septum before verifying calibration.</td>
</tr>
<tr>
<td>5. Plug septum assembly into intake filter housing.</td>
<td>5. See illustration, Page B-2.</td>
</tr>
<tr>
<td>6. Attach clean air filter to septum assembly.</td>
<td></td>
</tr>
<tr>
<td>7. Press POWER ON.</td>
<td></td>
</tr>
<tr>
<td>8. Note temperature of calibration vessel.</td>
<td></td>
</tr>
<tr>
<td>9. Inject 1 cc of mercury vapor according to the technique described on Page B-4.</td>
<td>9. Note: To minimize error, it is important to carefully follow this procedure.</td>
</tr>
<tr>
<td>10. Record meter reading.</td>
<td></td>
</tr>
</tbody>
</table>

B-1
11. Repeat Step 9 three times.

12. Refer to chart, Page B-5 for acceptable range and compare to Model 411 meter display.


14. Adjust BRIDGE BALANCE using trimmer tool until meter reads between 03 and 05.

15. Repeat calibration procedure, Steps 8-12.

11. The three 1 cc injections should be within ±5% of each other. If not, refer to Page B-4 for proper syringe technique and repeat procedure.

12. The average of the three meter readings obtained in Step 11 should fall within the range indicated in the chart. If so, the model 411 is in calibration. If the meter reading is not within range, proceed to the next step.


15. If meter reading is still not within range, refer to Page 18 of Jerome Instrument Corporation Model 411 Gold Film Analyzer Manual, "Trouble Shooting Calibration" or call Jerome Instrument Corporation customer service at (800) 952-2566.
Replace the Filter Disc after 20 hours of sampling. In environments containing a great deal of dust, the Filter Disc may need replacement as often as once a day.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Unscrew the Intake Filter Housing from the Model 411.</td>
<td></td>
</tr>
<tr>
<td>2. Remove Disc by pushing out with Trimmer Tool.</td>
<td></td>
</tr>
<tr>
<td>3. Replace with new Disc.</td>
<td>3. Avoid touching new Disc with fingers.</td>
</tr>
<tr>
<td>4. Screw the Intake Filter Housing back on the Model 411.</td>
<td></td>
</tr>
</tbody>
</table>
1. Check bar-stop setting (1 cc)

2. Insert needle into calibration vessel

3. Pump plunger 3 times

4. Pull plunger quickly and smoothly to bar-stop

5. Hold plunger firmly against bar-stop and remove syringe from vessel

6. Insert syringe needle to septum

7. Press SAMPLE

8. Release plunger so that gravity feeds Hg vapor into 411 airstream. Aid if necessary, by pushing plunger completely closed

9. Remove syringe needle from septum
**TEMPERATURE CONVERSION CHART - MODEL 411**

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Meter Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>.064 to .086</td>
</tr>
<tr>
<td>17</td>
<td>.070 to .094</td>
</tr>
<tr>
<td>18</td>
<td>.076 to .090</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>.082 to .112</td>
</tr>
<tr>
<td>20</td>
<td>.090 to .122</td>
</tr>
<tr>
<td>21</td>
<td>.097 to .131</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>.105 to .143</td>
</tr>
<tr>
<td>23</td>
<td>.115 to .155</td>
</tr>
<tr>
<td>24</td>
<td>.124 to .168</td>
</tr>
</tbody>
</table>
FILM HEAT PROCEDURE

Heat films after each day of use. Line voltage must be between 115 and 120 VAC for the films to clean properly. (For 230 VAC models, line voltage must be between 230 and 240 VAC.)

**Procedure**

1. Attach clean air filter to intake filter housing.
2. Attach line cord to 411 and plug into VAC outlet.
3. Connect battery charger to 411 and plug into VAC outlet.
4. Press POWER ON.
5. Press FILM HEAT.
6. Press SENSOR STATUS and hold down.
7. Adjust BRIDGE BALANCE using the trimmer tool until between 03 and 05.
8. Press POWER OFF.

**Comments**

1. Prevents mercury in the atmosphere from entering the Model 411.
2. The line cord is used only during FILM HEAT to provide line voltage to the films.
3. Ensures completion of FILM HEAT, even if batteries are low. The battery charger supplies operating voltage to the instrument. **CAUTION:** If LOW BAT is ON, charge batteries at least one hour before activating film heat.
5. Disregard any SENSOR STATUS reading at this time.
6. If >05 turn BRIDGE BALANCE clockwise; if <05 turn BRIDGE BALANCE counter-clockwise. **IMPORTANT:** The BRIDGE BALANCE should be adjusted ONLY AFTER A FILM HEAT CYCLE or if the METER READS L L L.
9. Disconnect battery charger and line cord.

10. Remove clean air filter.

11. Model 411 is ready for sampling.

12. Refer to chart, page B-5 for acceptable range and compare to Model 411 meter display.

12. The average of the three meter readings obtained in step 11 should fall within the range indicated in the chart. If so, the Model 411 is in calibration. If the meter reading is not within range, proceed to the next step.


14. Adjust BRIDGE BALANCE using trimmer tool until meter reads between 03 and 05.

15. Repeat calibration procedures, steps 8-12.

15. If meter reading is still not within range, refer to page 18 of Jerome Instrument Corporation Model 411 Gold Film Analyzer Manual, "Trouble Shooting Calibration" or call Jerome Instrument Corporation customer service at (800) 952-2566.

NOTE: If FILM HEAT is accidentally activated without the line cord being plugged in, there is no voltage to the film chamber. Discontinue cycle (POWER OFF), and restart (POWER ON).
**INTAKE FILTER DISC**

Replace the Filter Disc after 20 hours of sampling. In environments containing a great deal of dust, the Filter Disc may need replacement as often as once a day.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Unscrew the Intake Filter Housing Model 411.</td>
<td></td>
</tr>
<tr>
<td>2. Remove Disc by pushing out with Trimmer Tool.</td>
<td></td>
</tr>
<tr>
<td>3. Replace with new Disc.</td>
<td>3. Avoid touching new Disk with fingers.</td>
</tr>
<tr>
<td>4. Screw the Intake Filter Housing back on the Model 411.</td>
<td></td>
</tr>
</tbody>
</table>

WDR436/045.50
Outside View - Model 411

Intake Filter Housing

Low Bat

Survey 1 Sec

Sample 10 Sec

Sensor Status %

Power On/Off

Film Heat

Bridge Balance Pot

DataMate Receptacle

Battery Charger Receptacle

Line Cord Receptacle

AR300735
APPENDIX C
SUBCONTRACT LABORATORY
REPORT DESCRIPTIONS AND ORDER OF DATA DELIVERABLES
SUBCONTRACT LABORATORY

REPORT DESCRIPTIONS AND
ORDER OF DATA DELIVERABLES

The analytical and reporting requirements specified in this Attachment shall apply equally and individually to each group of samples received by LABORATORY, i.e.: each set of samples shall require the full complement of analysis, QA/QC and reporting requirements at the rate and type specified in each Order document. If any requirements contained within this Attachment conflict with instructions received in a specific Order document, the specific Order document (CRF) shall take precedence.

LABORATORY shall provide reports and other deliverables as specified below. Also reports and documentation MUST BE:

- Legible
- Clearly labeled and complete in accordance with instructions contained herein
- Arranged in the order specified in this section
- Paginated
- Single-sided

If submitted documentation does not conform to the above criteria, LABORATORY will be required to resubmit such documentation with all deficiencies corrected at its own expense. Whenever the laboratory is required to submit or resubmit data as a result of a Regional or SMO data review, the data must be sent to all contractual data recipients.

SAMPLE TRAFFIC REPORTS/PACKING LISTS

LABORATORY shall return to Viar the original traffic report/packing list page marked "Lab Copy for Return to SMO" with lab receipt information and signed in original signature, for each sample within five (5) days of receipt of last sample at laboratory each week (Monday through Saturday) for each Order document (CRF).

LABORATORY shall submit a Cover Sheet for each set of samples as described above. This cover sheet shall contain the following items:

- Lab name
- Contract number
- Sample analysis price—sample price from subcontract order

C-1

AR300737
List of Sample Numbers of all samples received with the week by the laboratory for each Order document, identifying the first and last samples received, and their dates of receipt (LRDs)

SAMPLE DATA PACKAGE

LABORATORY shall supply a sample data package that includes all analytical data for, but not limited to, field samples, reanalyses, blanks, matrix spikes, duplicates and/or matrix spike duplicates, preanalysis spikes or startup tests (if applicable), QC check samples and laboratory control samples, EPA references samples for the subject analyses as described in each Order document (CRF).

LABORATORY's sample data package shall be complete before submission, must be consecutively paginated (front to back).

LABORATORY shall arrange sample data forms in increasing EPA Sample Number order.

LABORATORY shall supply a cover page for each data package. The cover page shall include:

- Date of report
- Laboratory name and code
- Viar Prime contract number
- SAS Subcontract number, including suffix
- Client Request form number (if supplied)
- Laboratory QC report number
- EPA sample numbers in alphanumeric order cross referenced to laboratory ID number
- Definitions of laboratory data qualifiers

LABORATORY shall supply a case narrative with each data package. The case narrative shall include:

- SAS number without suffix
- Number and matrix of samples received
- Date of sample receipt
- Methods used for the analysis of samples
- Any deviations from required methods
Instrument identification and operating conditions

Problems encountered during sample receipt and/or analysis and decision tree process used

The following statement verbatim: "I certify that this data package is in compliance with the terms and conditions of the contract, both technically and for completeness, for other than the conditions detailed above. Release of the data contained in this data package has been authorized by the Laboratory Manager or his designee, as verified by the following signature." This statement shall be directly followed by signature of the Laboratory Manager or his designee with a typed line below it containing the signer's name and title, and the date of signature.

Copies of all telephone record logs that document conversations regarding the particular project.

LABORATORY shall supply summary data forms for analytical (field) samples, laboratory blanks, spikes, duplicates and/or spike duplicates, laboratory control samples, QC check samples, calibrations, detection limits, surrogate recoveries, and holding time information.

LABORATORY shall supply raw data (i.e., strip charts, chromatograms, quantitation reports, etc.) for samples, blanks, spikes, duplicates and/or spike duplicates, laboratory control samples, QC check samples, calibrations and tunes as generated by instrument readout. If no instrument readout or recorder paper is produced, LABORATORY must submit bench sheets with hand-written instrument readings (including sample preparation and/or digestion logs) with each sheet having the analyst's name and signature on it. All raw data supplied by the laboratory must contain the corresponding EPA sample number, date and time of analysis, instrument identification number and laboratory file identification number.

LABORATORY shall supply analysis/run logs indicating the sequence of all analyses including standards, sample, blanks, etc.

LABORATORY shall supply at least one example calculation showing how final result was obtained from raw data for each analyte.

LABORATORY shall supply copies of the following sample documentation, signed and dated, indicating receipt of samples:

- SAS Packing List/Traffic Reports
- Chain-of-Custody
LABORATORY shall supply a copy of each specific Order document in each of its corresponding data packages. LABORATORY must also include copies of any methods supplied with each Order document in the data package. The methods should include standard operating procedures for sample preparation and analysis.

LABORATORY shall retain a copy of the sample data package for 365 days after final submission of data. After this time, the laboratory may dispose of the package.

CLIENT SAMPLE DATA FILE (CSF)

LABORATORY shall supply one Client Sample Data File (CSF) to be delivered to the Regional client concurrently with delivery of the Sample Data Package to Viar.

The CSF will consist of the following original documents in addition to the documents in the Sample Data Package. The contents of the CSF will be consecutively numbered. No copies will be placed in the CSF unless the originals are bound in a logbook which is maintained by the laboratory.

1. A completed and signed Document Inventory Sheet (Form DC-2).

2. All original shipping documents, including, but not limited to, the following documents:
   - Chain-of-Custody Record(s)
   - Airbills
   - Traffic Report(s)/Packing List(s)
   - Sample Tags (if present) sealed in plastic bags

3. All original receiving documents, including, but not limited to, the following documents:
   - Form DC-1
   - Other receiving forms or copies of receiving logbooks
   - Cover sheet for traffic report(s)/packing list(s)

4. All original laboratory records, not already submitted in the Sample Data Package, of sample transfer, preparation and analysis, including, but not limited to, the following documents:
   - Original preparation and analysis forms or copies of preparation and analysis logbook pages.
   - Internal sample and sample extract transfer chain-of-custody records.
5. All other original SDG-specific documents in the possession of the laboratory, including, but not limited to, the following documents:

- Telephone contact logs
- Copies of personal logbook pages
- All handwritten project-specific notes
- Any other project-specific documents not covered by the above

All documentation related to a particular project may be used or admitted as evidence in subsequent legal proceedings. Any other project-specific documents generated after the CSF is sent to EPA, as well as copies that are altered in any fashion, are also deliverables to EPA. If the laboratory does not submit project-specific documents to EPA after submission of the CSF, the documents should be numbered as an addendum to the CSF and a revised DC-2 form should be submitted, or the documents should be numbered as a new CSF and a new DC-2 form should be submitted (Original to the Region and copies to Viar).

ORDER OF DATA DELIVERABLES

LABORATORY shall supply data to all data recipients concurrently in the format listed below:

**Type I**
(data for samples analyzed using GC, GC/MS, HRMS, GC/MS/MS HPLC, LC/MS)

The data package shall include the following items in the following order:

1. Summary data package (Viar package only)
2. Inventory sheet (Form DC-2)
3. Cover page
4. Narrative
5. Copy of the Order document (SAS client request form)
6. Copies of traffic reports/packing lists
7. QC summary forms
8. Raw sample data
9. Raw standards data
10. Raw QC data
11. CSF (regional package only)
12. Sample number as per the paperwork
Type II
(all other types of data)

The data package shall include the following items in the following order:

1. Summary data package (Viar package only)
2. Inventory sheet (Form DC-2)
3. Cover page
4. Narrative
5. Summary forms for samples, standards, and QC
6. Raw data for standards, and QC
7. Sample preparation logs
8. Copies of traffic reports/packing lists
9. Copy of the Order document
10. CSF (regional package only)
11. Sample number as per the paperwork

LABORATORY shall retain a copy of the complete sample data package (summary data package, sample data package and CSF) for 365 days after final submission of data. After this time, the laboratory may dispose of the package.

SUMMARY FROM CRL/EPA

Data package must include: all raw data, all instrument and/or equipment calibration results, calculations, blank results, duplicate results, chain-of-custody forms, SAS request forms, SAS packing list(s) or traffic report(s), copy of airbill(s), and copies of analyst's logbooks (signed by analyst) with date and time of sample preparation and analysis.

The cover page and all sample report forms MUST be labeled with the complete EPA sample number as it appears on chain-of-custody and CLP paperwork.

The case narrative must document all problems encountered and the subsequent resolutions. List instrumentation and methods employed for analysis. Also, note whether samples were preserved or not and the procedure utilized in preservation. EPA QC reference samples, or equivalent reference samples must be identified as to source and lot number. Documentation of "true" value and associated 95 percent confidence limits must be provided for any reference samples used.

WDCR468/029.51
APPENDIX D

SPECIAL ANALYTICAL SERVICES REQUESTS
FOR
TOTAL MERCURY ANALYSIS OF GROUNDWATER
AND
TOTAL MERCURY ANALYSIS OF SOIL AND WASTE
SPECIAL ANALYTICAL SERVICES
Regional Request

[X] Regional Transmittal [ ] Telephone Request

A. EPA Region and Client: EPA Region III/CH2M HILL
B. Regional Representative: Colleen K. Walling
C. Telephone Number: (301) 266-9190
D. Date of Request: April 6, 1990

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

1. General description of analytical service requested:
Analysis of groundwater for total mercury using SW-846, Method 7470 with some modifications (attached).

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or Soil and sediments; and whether low, medium, or high concentrations):
Approximately twelve (12) groundwater samples for total mercury using SW-846, Method 7470 with some modifications (attached). All samples will be low level concentration. Unit count includes required duplicate and spike duplicate. Unit count does not include calibration standards or laboratory method blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, ETC.):
Superfund enforcement.
4. Estimated date(s) of collection:
The approximate date of collection is April 23, 1990. However, the PRP is waiting for the proper equipment before starting the sampling and will give CH2M HILL two weeks notice before sampling takes place. The EPA Regional Representative will also be contacted two weeks before sampling takes place.

5. Estimated date(s) and method of shipment:
Samples will be shipped by overnight carrier the day of collection. See estimated date of collection for explanation of sampling date.

6. Approximate number of days results required after lab receipt of samples:
Samples must be analyzed within 14 days of VTSR. Completed data package required by 30 days of receipt of last sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
Analyze all samples using SW-846, Method 7470 with some modifications (attached). The detection limit of the method is 0.20 ug Hg/L. Analyze one duplicate sample and one matrix spike for every 10 samples (or per batch if fewer than 10 samples total). Verify calibration with an independently prepared check standard. Prepare calibration curves as given in Method 7470.

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

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of Custody documentation, etc.). If not completed, format of results will be left to program discretion.
Follow data package format of CLP, Statement of Work for Inorganic Analysis (revision of 7/88). Include all analyst logbook pages, run logs, raw data, calculations, data summary sheets, chain-of-custody (including laboratory chronicle forms that document sample custody within the laboratory), dates of sample analyses, copies of SAS packing lists, and airbills. Individual pages of the data packages must be numbered. All report forms and data must be labeled with EPA sample number as per chain-of-custody and CLP forms. Results are to be reported in ug Hg/L. Records of analysis and calculations must be legible and sufficient to recalculate all concentrations. EPA or NBS QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot
number, and sample number. Corresponding "true" or target values and associated 95 percent confidence limits for analysis results will be provided for all reference samples used.

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

11. Name of sampling/shipping contact: Tom McLaughlin
   Phone: (703) 471-1441

12. DATA REQUIREMENTS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Detection Limit</th>
<th>Precision Desired (+/- % or conc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Mercury</td>
<td>0.20 ug Hg/L</td>
<td>+/- 20%</td>
</tr>
</tbody>
</table>

13. QUALITY CONTROL REQUIREMENTS

All QA/QC requirements shall be performed and reported as specified in CLP SOW for Inorganics Analysis (7/88). Follow procedures for quality control as given in Method 7470. Duplicates and matrix spikes should be analyzed as stated in the Analytical Protocol Required.

14. Action Required if Limits are Exceeded:

Contact Colleen K. Walling, U.S. EPA, and Tom McLaughlin, CH2M HILL.

15. Request prepared by: Tom McLaughlin/CH2M HILL
   Date: April 3, 1990

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.
METHOD 7470

MERCUry IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.
3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.
Figure 1. Apparatus for flameless mercury determination.
4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M KMnO₄ and 10% H₂SO₄; or
2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid (H₂SO₄), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO₃), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H₂SO₄. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.) (See page 7470-7)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.) (See page 7470-7)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of Type II water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of Type II water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of Type II water. Add 10 mL of concentrated HNO₃ and adjust the volume to 100.0 mL (1 mL = 1 mg Hg).

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 g per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.
6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO₃. The suggested maximum holding times for these samples are 38 days in glass containers and 13 days in plastic containers.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 g of mercury, to a 300-mL BOD bottle. Add 5 mL of H₂SO₄ and 2.5 mL of concentrated HNO₃, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H₂SO₄ and 2.5 mL of concentrated HNO₃ to each bottle. Add 15 mL of KMnO₄ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and
continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES


SECTION 5.0 REAGENTS (continued)

Stannous Chloride, SnCl₂: 10 percent W/V; dissolve 119 grams of reagent grade SnCl₂ 2H₂O in 40 ml of concentrated hydrochloric acid and dilute to a liter volume with D.I. water.

Hydroxylamine hydrochloride, H₂NOH HCl: 4% W/V, dissolve 20 grams of reagent grade H₂NOH HCl in 60-70 ml D.I. water. Adjust the pH of the solution to 2.8 ± 0.2 with ammonium hydroxide, NH₄OH. Add 10 ml of a 4% sodium diethyldithiocarbamate solution to complex any metallic impurities. After five minutes, extract the metallic impurities with 20 ml of chloroform in a separatory funnel. Repeat the chloroform extraction twice discarding the chloroform layer after each extraction. Adjust the pH of the aqueous layer to 1.2 with hydrochloric acid and dilute to 500 ml volume with D.I. water.
METHOD 7470

- MERCURY (MANUAL COLD-VAPOR TECHNIQUE)

Start

7.1
Prepare sample

7.2
Transfer aliquots of mercury working standard to series of bottles for standard preparation

7.2
Add Type II water to each bottle; mix; add conc. H_2SO_4 and KMnO_4

7.2
Add KMnO_4 solution; add potassium peroxalate; heat; cool

7.3
Reduce excess permanganate; attach to aeration apparatus

7.3
For analysis, run circulating pump continuously, aerate

7.3
Construct calibration curve; determine peak height and mercury value

7.5
Analyze by method of standard additions

7.5
 Routinely analyze duplicates, spiked samples, and check standards

7.6
Calculate metal concentrations

Stop

Revision 0
Date September 1986

7470 - 8

AR300754
SPECIAL ANALYTICAL SERVICES
Regional Request

[X] Regional Transmittal [ ] Telephone Request

A. EPA Region and Client: EPA Region III/CH2M HILL
B. Regional Representative: Colleen K. Walling
C. Telephone Number: (301) 266-9190
D. Date of Request: April 6, 1990

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

1. General description of analytical service requested:
   Analysis of soil and waste for total mercury using Sw-846, Method 7471 with some modifications (attached).

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or Soil and sediments; and whether low, medium, or high concentrations):
   Approximately four (4) soil and five (5) waste samples for total mercury using SW-846, Method 7471 with some modifications (attached). All samples will be low level concentration. Unit count includes required duplicate and spike duplicate. Unit count does not include calibration standards or laboratory method blanks.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, ETC.):
   Superfund enforcement.
4. Estimated date(s) of collection:
The approximate date of collection is April 23, 1990. However, the PRP is waiting for the proper equipment before starting the sampling and will give CH2M HILL two weeks notice before sampling takes place. The EPA Regional Representative will also be contacted two weeks before sampling takes place.

5. Estimated date(s) and method of shipment:
Samples will be shipped by overnight carrier the day of collection. See estimated date of collection for explanation of sampling date.

6. Approximate number of days results required after lab receipt of samples:
Samples must be analyzed within 14 days of VTSR. Completed data package required by 30 days of receipt of last sample.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
Analyze all samples using SW-846, Method 7471 with some modifications (attached). The detection limit of the method is 0.1 ug Hg/g. Analyze one duplicate sample and one matrix spike for every 10 samples (or per batch per matrix if fewer than 10 samples total). Verify calibration with an independently prepared check standard. Prepare calibration curves as given in Method 7471.

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

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of Custody documentation, etc.). If not completed, format of results will be left to program discretion.
Follow data package format of CLP, Statement of Work for Inorganic Analysis (revision of 7/88). Include all analyst logbook pages, run logs, raw data, calculations, data summary sheets, chain-of-custody (including laboratory chronicle forms that document sample custody within the laboratory), dates of sample analyses, copies of SAS packing lists, and airbills. Individual pages of the data packages must be numbered. All report forms and data must be labeled with EPA sample number as per chain-of-custody and CLP forms. Results are to be reported in ug Hg/g. Records of analysis and calculations must be legible and sufficient to recalculate all concentrations. EPA or NBS QC
reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95 percent confidence limits for analysis results will be provided for all reference samples used.

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

11. Name of sampling/shipping contact: Tom McLaughlin
   Phone: (703) 471-1441

12. DATA REQUIREMENTS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Detection Limit</th>
<th>Precision Desired (+/- % or conc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Mercury</td>
<td>0.1 ug Hg/g</td>
<td>+/- 20%</td>
</tr>
</tbody>
</table>

13. QUALITY CONTROL REQUIREMENTS
All QA/QC requirements shall be performed and reported as specified in CLP SOW for Inorganics Analysis (7/88). Follow procedures for quality control as given in Method 7471. Duplicates and matrix spikes should be analyzed as stated in the Analytical Protocol Required.

14. Action Required if Limits are Exceeded:
Contact Colleen K. Walling, U.S. EPA, and Tom McLaughlin, CH2M HILL.

15. Request prepared by: Tom McLaughlin/CH2M HILL
   Date: April 6, 1990

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.
1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.
4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the
Figure 1. Apparatus for flameless mercury determination.
system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M KMnO₄ and 10% H₂SO₄, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO₃.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate. (See page 7471-7)

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate. (See page 7471-7)

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of Type II water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of Type II water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 μg/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.
6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with nitric acid.

6.4 For solids or semisolids, moisture may be driven off in a drying oven at a temperature of 60°C.

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of Type II water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL of Type II water and 15 mL of potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, as Cl2 could be evolved. Add 55 mL of Type II water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H2SO4 and 2 mL of concentrated HNO3 are added to the 0.2 g of sample. Add 5 mL of saturated KMnO4 solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with Type II water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 μg of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL of Type II water and 15 mL of KMnO4 solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of Type II water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.
7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.6 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.
9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES


SECTION 5.0 REAGENTS (continued)

Stannous Chloride, SnCl₂: 10 percent W/V; dissolve 119 grams of reagent grade SnCl₂·2H₂O in 40 ml of concentrated hydrochloric acid and dilute to a liter volume with D.I. water.

Hydroxylamine hydrochloride, N₂NOH HCl: 4% W/V, dissolve 20 grams of reagent grade H₂NOH HCl in 60-70 ml D.I. water. Adjust the pH of the solution to 2.8 ± .2 with ammonium hydroxide, NH₄OH. Add 10 ml of a 4% sodium diethyl-dithiocarbamate solution to complex any metallic impurities. After five minutes, extract the metallic impurities with 20 ml of chloroform in a separatory funnel. Repeat the chloroform extraction twice discarding the chloroform layer after each extraction. Adjust the pH of the aqueous layer to 1.2 with hydrochloric acid and dilute to 500 ml volume with D.I. water.

SECTION 7.0 PROCEDURES (continued)

7.25 Sample Preparation: Weigh 2-5 grams of untreated sample and place into a 100 ml volumetric flask. Add 10 ml of Type II water and 15 ml aqua regia slowly. Heat 2 minutes in a water bath at 95°C. Cool; then add an excess of potassium permanganate solution to each sample. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and reduce excess permanganate solution with hydroxylamine hydrochloride solution, add 2 ml excess. Dilute to volume with Type II water. Pipet appropriate volume into a BOD and adjust volume to 125 ml with Type II water. Continue as described under step 7.4.
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<th>Sample Matrix</th>
<th>Preparation Method</th>
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<td>Emission control dust</td>
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<tr>
<td>Wastewater treatment sludge</td>
<td>Not known</td>
<td>0.4, 0.28 ug/g</td>
</tr>
</tbody>
</table>
ALTERNATIVE REMEDIAL CONTRACTING STRATEGY PROGRAM
FIELD SAMPLING PLAN
SALTVILLE RI/FS OVERSIGHT

EPA CONTRACT NO. 68-W8-0090
EPA WORK ASSIGNMENT NO.: 90-09-3L24
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WDCR45/003.51
ACRONYMS AND ABBREVIATIONS

COC  -  Chain-of-Custody
DQO  -  Data Quality Objective
EPA  -  Environmental Protection Agency
FS   -  Feasibility Study
FSP  -  Field Sampling Plan
PRP  -  Potentially Responsible Party
QC   -  Quality Control
RI   -  Remedial Investigation
SAP  -  Sampling and Analysis Plan
SM   -  Site Manager
SOW  -  Statement of Work

WDCR45/015.50

AR300770
This field sampling plan (FSP) describes the scope of sample collection activities to be performed by CH2M HILL in the oversight of the Saltville Remedial Investigations (RIs) for Operable Unit 2 (soil, water, and groundwater), and for Operable Unit 3 (bioassessment). These oversight sampling activities include the collection of splits of groundwater, soil, and waste samples in the field and the collection of homogenized splits of PRP samples for several media, specifically:

- Fish
- Benthic Macroinvertebrates
- Mussels

These split samples will be generated after homogenization by the PRP's laboratory. The purpose of collecting these samples is to provide data that will be used to compare the PRP analytical results to the corresponding analytical results of the split samples from the Oversight Analytical Laboratory.

In addition to collecting split samples, CH2M HILL field oversight personnel will observe PRP sample collection to assess whether samples are being collected in accordance with the PRP's approved SAP. If deviations from the SAP are observed, the RPM will be contacted. Field oversight personnel will have knowledge of and have on site the PRP's workplan and SAP.

1.1 OBJECTIVES

The objective of the sampling effort is to collect representative split samples that meet the data quality objectives (DQOs) set forth in the QAPjP that can be used to determine the comparability of the Oversight Analytical Laboratory results with the corresponding analytical results from the PRP's analytical laboratory.

The objectives of this FSP are to identify:

1. The number of split samples to be collected

2. The procedures to be used in the field to collect splits of groundwater, soil, and waste samples
3. The procedures to be used to assume custody of homogenized split samples in the PRP analytical laboratory.

4. The procedures to be used for adequate quality control

5. The procedures for chain-of-custody (COC) protocols and documentation of sample collection activities

For convenience, the oversight sampling activities for all of the media are summarized in Table 1-1.

WDCR45/001.51
**Table 1-1
SUMMARY OF SAMPLING PROGRAM**

<table>
<thead>
<tr>
<th>Media</th>
<th>Analysis</th>
<th>No. of Samples</th>
<th>Field Blank</th>
<th>Additional Volume Needed for Lab QA/QC Samples (Total Mercury)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater</td>
<td>Total Mercury</td>
<td>40(^b)</td>
<td>1/day</td>
<td>Double volume per 10 samples or at least one each sampling event</td>
</tr>
<tr>
<td>Waste</td>
<td>Total Mercury</td>
<td>2</td>
<td>None</td>
<td>Double volume per 10 samples or at least one each sampling event</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>2</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Soil</td>
<td>Total Mercury</td>
<td>3</td>
<td>None</td>
<td>Double volume per 10 samples or at least one each sampling event</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>3</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Fish</td>
<td>Total Mercury</td>
<td>40-80(^b)</td>
<td>None</td>
<td>Double volume per 10 samples or at least one each sampling event</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>40-80(^b)</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Macroinvertebrates</td>
<td>Total Mercury</td>
<td>10(^b)</td>
<td>None</td>
<td>Double volume per 10 samples or at least one each sampling event</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>10(^b)</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Mussels</td>
<td>Total Mercury</td>
<td>26(^b)</td>
<td>None</td>
<td>Double volume per 10 samples or at least one each sampling event</td>
</tr>
<tr>
<td></td>
<td>Methyl Mercury</td>
<td>26(^b)</td>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)No splits will be collected of samples analyzed as a part of the bioaccumulation study.

\(^b\)One split per 20 samples collected by PRP.

WDCR45/011.50
Section 2
SAMPLING PLAN FOR FISH

The PRP's Field Sampling Plan for Fish (October 1989), Section 2.3.2, specifies the fish samples to be collected by the PRP during the study. Splits of the samples collected by the PRP will be obtained after homogenization in the PRP laboratory. CH2M HILL will assume custody of the homogenized split sample in the laboratory as described later in this section.

2.1 SUMMARY OF PRP ACTIVITIES

The PRP will conduct fish surveys at six stations sited on the NFHR between Mile 100 and Mile 53. The surveys will be conducted in the spring and early fall over a 2-year period. The PRP's sampling locations are shown in Figure 2-1 and are described in Table 2-1.

The fish will be collected using standard collection equipment, such as seines, minnow traps, and electroshockers. Fish will be collected, counted, and identified (if possible) in the field. Four species of fish—smallmouth bass, rock bass, channel catfish, and redbreasted sunfish—will be selected for analysis. The PRP will collect a minimum of 8 and a maximum of 16 fish of each species from each station for analysis.

The fish samples will be prepared by the PRP either in the field or in the laboratory. The fillet, the offal, and the scales, fins, and vertebrae will be separated and packaged separately in zip-lock plastic bags.

The reader is referred to the PRP's field sampling plan for a more detailed description of the field activities. The description in this section is not intended to provide detail sufficient for assessing PRP adherence to the approved SAP.

2.2 SAMPLE FREQUENCY

As directed by EPA Region III, CH2M HILL will collect splits of 5 percent of the samples collected by the PRP for analysis. Table 1-1 summarizes the splits of the fish samples which will be collected during the study. The sample collection procedures to be used by the PRP are...
<table>
<thead>
<tr>
<th>Site No.</th>
<th>Location</th>
<th>NFHR River Mile</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Old Broad Ford</td>
<td>91.5</td>
</tr>
<tr>
<td>2</td>
<td>Vicinity of McCready</td>
<td>85.6</td>
</tr>
<tr>
<td>3</td>
<td>Downstream of Pond 5 and Pond 6 Outfall</td>
<td>81.3</td>
</tr>
<tr>
<td>4</td>
<td>Former chloride-analyzer site</td>
<td>80.0</td>
</tr>
<tr>
<td>5</td>
<td>Downstream of Tumbling Creek - NFHR confluence</td>
<td>76.7</td>
</tr>
<tr>
<td>6</td>
<td>1.5 mi. east of Route 611 and Route 19 junction--Mongle Springs</td>
<td>61.0</td>
</tr>
</tbody>
</table>
described in the PRP’s Field Sampling Plan For Fish (October 1989). The PRP fish samples to be split will be selected by CH2M HILL’s oversight personnel. The split samples will be prepared (homogenized) by the PRP laboratory in accordance with the homogenization procedures in the PRP Field Sampling Plan (October 1989).

2.3 SAMPLE DESIGNATION

Each split sample will be assigned a unique sample identification number. The sample numbering system will be:

\[
\text{CH-Sxx-yyyyA-zz or CH-Sxx-yyyyF-zz}
\]

where

- CH is the designation for CH2M HILL split samples
- sxx is the site number
- yyyy is a four digit number (starting with 0001 with the first fish collected and assigned sequentially)
- A is for offal samples
- F is for fillet samples
- zz is the year collected (89 for 1989)

This numbering scheme corresponds to the PRP’s numbering scheme with the exception of the CH prefix, which distinguishes the split sample from the PRP’s original half of the sample.

2.4 COORDINATION OF COLLECTION WITH PRP LABORATORY

The interaction with the PRP laboratory to obtain splits of homogenized samples will be coordinated and pre-arranged through EPA Region III.

After homogenization by the PRP’s laboratory, the sample volume of the designated sample to be split will be divided into two equal portions. A representative of CH2M HILL will accept the split of the homogenized sample in a 6-oz glass jar (3 oz for methyl mercury and 3 oz for total mercury analysis). The container will then be tagged with the following information:

- Sample Number
- Species
- Sample Type (Fillet, Offal, Scales, etc.)
- Location
The sample container and tag will be placed in a 2-mil polyethylene bag. Tags should be positioned so they can be read through the bag.

If there is adequate volume, a duplicate sample will be obtained by dividing the split sample into two equal volumes.
Section 3

SAMPLING PLAN FOR BENTHIC MACROINVERTEBRATES

The PRP's Field Sampling Plan For Benthic Macroinvertebrates and Algae (October, 1989), Section 3.2, specifies the benthic macroinvertebrate samples to be collected by the PRP during the study. Splits of the samples collected by the PRP will be obtained after homogenization in the PRP laboratory. CH2M HILL will assume custody of the homogenized split sample in the laboratory as described later in this section.

3.1 SUMMARY OF PRP ACTIVITIES

The PRP will conduct qualitative surveys of algae and qualitative and quantitative surveys of benthic macroinvertebrates during the winter, spring, and fall. These surveys will be conducted to evaluate the status of the invertebrate and aquatic plant communities from NFHRM 100 to NFHRM 53. The sampling will be conducted over a 2-year period. The PRP's sampling locations are shown in Figure 3-1 and are described in Table 3-1.

Six quantitative Hess samples will be collected from the riffle areas, and one qualitative "kick" sample will be collected per site. Four samples will be used for quantitative analysis, and two will be used as QA/QC samples. Three samples of crayfish and megalopterans, if present, will be collected from each site for mercury and methylmercury analysis.

Insect samples will be collected during the spring and fall surveys, and algae samples will be collected for species identification with some samples for mercury and methylmercury analysis.

Benthic macroinvertebrate samples collected for mercury and methylmercury analysis will be packaged in zip-lock plastic bags, plastic containers, or glass jars.

The reader is referred to the PRP's field sampling plan for a more detailed description of the field activities. The description in this section is not intended to provide detail sufficient for assessing PRP adherence to the approved SAP.

Figure 3-1
PRP'S SAMPLING LOCATIONS FOR BENTHIC AND ALGAE MONITORING
Saltville Waste Disposal Site
Saltville RI/FS Oversight
<table>
<thead>
<tr>
<th>Site No.</th>
<th>Location</th>
<th>River Mile</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Old Broad Ford</td>
<td>91.5</td>
</tr>
<tr>
<td>2</td>
<td>Vicinity of McCready</td>
<td>85.6</td>
</tr>
<tr>
<td>3</td>
<td>Downstream of Pond 5 - left side of island</td>
<td>81.3</td>
</tr>
<tr>
<td>4</td>
<td>Former chloride-analyzer site</td>
<td>80.0</td>
</tr>
<tr>
<td>5</td>
<td>Downstream of Tumbling Creek--NFHR confluence</td>
<td>76.6</td>
</tr>
<tr>
<td>6</td>
<td>1.5 mi. east of Route 611 and Route 19 junction--Mongle Springs</td>
<td>61.0</td>
</tr>
</tbody>
</table>

WDCR45/021.50
3.2 SAMPLE FREQUENCY

As directed by EPA Region III, CH2M HILL will collect splits of 5 percent of the samples collected by the PRP for analysis. Table 1-1 summarizes the splits of the benthic macroinvertebrate samples that will be collected during the study. The sample collection procedures to be used by the PRP are described in the PRP's Field Sampling Plan For Benthic Macroinvertebrates and Algae (October, 1989). The PRP benthic macroinvertebrate samples to be split will be selected by CH2M HILL's oversight personnel. The split samples will be prepared (homogenized) by the PRP laboratory in accordance with the homogenization procedures in the PRP Field Sampling Plan (October, 1989).

3.3 SAMPLE DESIGNATION

Each split sample will be assigned a unique sample identification number. The sample numbering system will be:

CH-Sxx-yyyyB-zz

where

CH is the designation for CH2M HILL split sample sxx is the site number

yyyy is a four digit number (starting with 0001 with the first benthic macroinvertebrate sample collected and assigned sequentially)

B is for benthic macroinvertebrate samples

zz is the year collected (89 for 1989)

This numbering scheme corresponds to the PRP's numbering scheme with the exception of the CH prefix, which distinguishes the split sample from the PRP's original half of the sample.

3.4 COORDINATION OF COLLECTION WITH PRP LABORATORY

The interaction with the PRP laboratory to obtain splits of homogenized samples will be coordinated and pre-arranged through EPA Region III.

After homogenization by the PRP's laboratory, the sample volume of the designated sample to be split will be divided into two equal portions. A representative of CH2M HILL will
accept the split of the homogenized sample in a 6-oz glass jar (3 oz for methyl mercury and 3 oz for total mercury analysis). The container will then be tagged with the following information:

- Sample Number
- Sampling Location
- Sampling Date and Time
- Species

The sample container and tag will be placed in a 2-mil polyethylene bag. Tags should be positioned so they can be read through the bag.

If there is adequate volume, a duplicate sample will be obtained by dividing the split sample into two equal volumes.
Section 4

SAMPLING PLAN FOR MUSSELS

The PRP's Field Sampling Plan For Mussels (October, 1989), Section 3.2, specifies the mussel samples to be collected by the PRP during the study. Splits of the samples collected by the PRP will be obtained after homogenization in the PRP laboratory. CH2M HILL will assume custody of the homogenized split sample in the laboratory as described later in this section.

4.1 SUMMARY OF PRP ACTIVITIES

The PRP will conduct mussel surveys in the spring of 1990. The survey will be conducted from NFHRM 92 to NFHRM 53 at regular intervals (approximately every 3 miles) and Asiatic clams from each mussel survey site (total of 13 sites) will be analyzed for total and methylmercury. The sites are located as shown in Figure 4-1.

Asiatic clams will be collected for sampling using hand-held nets and clam rakes. Three 10-gram composite tissue samples will be used from each site for analysis for mercury and methylmercury. The clams will be placed in zip-lock plastic bags.

The reader is referred to the PRP's field sampling plan for a more detailed description of the field activities. The description in this section is not intended to provide detail sufficient for assessing PRP adherence to the approved SAP.

4.2 SAMPLE FREQUENCY

As directed by EPA Region III, CH2M HILL will collect splits of 5 percent of the samples collected by the PRP for analysis. Table 1-1 summarizes the splits of the mussel samples that will be collected during the study. The sample collection procedures to be used by the PRP are described in the PRP's Field Sampling Plan For Mussels (October, 1989). The PRP mussel samples to be split will be selected by CH2M HILL's oversight personnel. The split samples will be prepared (homogenized) by the PRP laboratory in accordance with the homogenization procedures in the PRP Field Sampling Plan (October, 1989).
Former Chlorine Plant Site.

One Site Located Outside Mapped Area At NFRM 532 Not Shown.


Figure 4-1
PRP'S SAMPLE SITES FOR ASIATIC CLAMS AND MUSSELS Saltville Waste Disposal Site Saltville RI/FS Oversight
4.3 SAMPLE DESIGNATION

Each split sample will be assigned a unique sample identification number. The sample numbering system will be:

CH-Sxx-yyyySM-zz or CH-Sxx-yyyyFM

where

CH is the designation for CH2M HILL split sample
sxx is the site number
yyyy is a four digit number (starting with 0001 with the first mussel sample collected and assigned sequentially)
S/F is the season of collection (summer or fall)
M is the designation for mussel sample
zz is the year collected (89 for 1989)

This numbering scheme corresponds to the PRP's numbering scheme with the exception of the CH prefix, which distinguishes the split sample from the PRP's original half of the sample.

4.4 COORDINATION OF COLLECTION WITH PRP LABORATORY

The interaction with the PRP laboratory to obtain splits of homogenized samples will be coordinated and pre-arranged through EPA Region III.

After homogenization by the PRP's laboratory, the sample volume of the designated sample to be split will be divided into two equal portions. A representative of CH2M HILL will accept the split of the homogenized sample in a 6-oz glass jar (3 oz for methyl mercury and 3 oz for total mercury analysis). The container will then be tagged with the following information:

- Sample Number
- Species
- Sampling Location
- Sampling Date and Time

The sample container and tag will be placed in a 2-mil polyethylene bag. Tags should be positioned so they can be read through the bag.
If there is adequate volume, a duplicate sample will be obtained by dividing the split sample into two equal volumes.
The PRP's Field Sampling Plan For Groundwater Studies (October, 1989), Section 3.2, specifies the groundwater samples to be collected by the PRP during the study. Splits of the samples collected by the PRP will be obtained by CH2M HILL oversight personnel in the field.

5.1 SUMMARY OF PRP ACTIVITIES

The PRP will collect groundwater samples from clustered monitoring wells at 10 locations. In addition, the PRP will collect samples at the chlorine plant site well and surface water samples at the inlet to the pond outfall structure, the pond outfall, and the western diversion ditch. The samples will be collected according to the frequency shown in Table 5-1. The monitoring well locations are shown in Figure 5-1.

Water-level measurements will be taken, and the well will be purged with a "WaTerra" brand inertial pump (foot valve) or a dedicated bailer. After a sufficient volume of water has been purged from the well, the sample will be collected and placed in an appropriate sample bottle.

The reader is referred to the PRP's field sampling plan for a more detailed description of the field activities. The description in this section is not intended to provide detail sufficient for assessing PRP adherence to the approved SAP.

5.2 SAMPLE FREQUENCY

As directed by EPA Region III, CH2M HILL will collect splits of 5 percent of the samples collected by the PRP for analysis. Table 1-1 summarizes the splits of the groundwater samples that will be collected during the study. The sample collection procedures to be used by the PRP are described in the PRP's Field Sampling Plan For Groundwater Studies (October, 1989). The PRP groundwater samples to be split will be selected by CH2M HILL's oversight personnel. The split samples will be obtained in the field immediately after sample collection by the PRP.
<table>
<thead>
<tr>
<th>Sample Point</th>
<th>Hg</th>
<th>MeHg</th>
<th>Metals</th>
<th>Vol</th>
<th>SV</th>
<th>Pest</th>
<th>Field</th>
<th>Geo</th>
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<tbody>
<tr>
<td>MW-1</td>
<td>Q</td>
<td>I</td>
<td>I</td>
<td>Q</td>
<td>Q</td>
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<td>Q</td>
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<td>MW-2</td>
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<td>I</td>
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<td>I</td>
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<td>I</td>
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<td>I</td>
<td>Q</td>
<td>I</td>
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<td>Q</td>
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<td>Q</td>
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<tr>
<td>PI-5</td>
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<td>I</td>
<td>I</td>
<td>Q</td>
<td>Q</td>
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**NOTES:**
- **MW** - Monitoring Well
- **CP** - Chlorine Plant Site Well
- **PI** - Inlet to Pond Outfall Structure
- **PO** - Pond Outfall
- **WD** - Western Diversion Ditch
- **Hg** - Total Mercury by Method 245.1 CLP-M
- **MeHg** - Methylmercury
- **Metals** - Metals by Method 200.7 CLP-M
- **Vol** - Volatiles by CLP (VOA)
- **SV** - Semi-volatiles by CLP (SV)
- **Pest** - Pesticides by CLP (PEST)
- **Field** - Field-measured parameters:
  - pH
  - Conductivity
  - Temperature
Table 5-1 (Continued)

Notes:

Geo - Major ions for geo chemistry:

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<th>Analyte</th>
<th>Method</th>
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<tr>
<td>TDS</td>
<td>160.1</td>
</tr>
<tr>
<td>Na⁺⁺</td>
<td>200.7 CLP-M*</td>
</tr>
<tr>
<td>K⁺⁺</td>
<td>200.7 CLP-M*</td>
</tr>
<tr>
<td>Ca⁺⁺</td>
<td>200.7 CLP-M*</td>
</tr>
<tr>
<td>Mg⁺⁺</td>
<td>200.7 CLP-M*</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>Standard Method 429**</td>
</tr>
<tr>
<td>F⁻</td>
<td>Standard Method 429**</td>
</tr>
<tr>
<td>Br⁻</td>
<td>Standard Method 429**</td>
</tr>
<tr>
<td>S⁰⁴⁻</td>
<td>Standard Method 429**</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>310.0</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>Standard Method 429**</td>
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<tr>
<td>I⁻</td>
<td>Standard Method 429**</td>
</tr>
<tr>
<td>S⁻⁻</td>
<td>Standard Method 429**</td>
</tr>
</tbody>
</table>

* Inductively coupled plasma (ICP)
** Ion Chromatography

Q - Quarterly
I - First Sampling; subsequent sampling to be based on results of initial sample
D - Daily (5 days/week)
W - Weekly

Sample points PI and WD are intermittent stormwater runoff to be sampled when flowing.

WDCR45/022.51
5.3 SAMPLE DESIGNATION

Each split sample will be assigned a unique sample identification number. The sample numbering system will be:

CH-MWxxxx-Dxxxxxx

where

CH is the designation for CH2M HILL split sample
MWxxxxxx is the monitoring well number
Dxxxxxx is the date of sampling.

This numbering scheme corresponds to the PRP's numbering scheme with the exception of the CH prefix, which distinguishes the split sample from the PRP's original half of the sample.

5.4 COORDINATION OF COLLECTION WITH PRP FIELD PERSONNEL

The interaction with the PRP field personnel to obtain the split samples will be coordinated and pre-arranged through EPA Region III.

After the sample is collected by the PRP field personnel, from the designated location for collection of the split sample, a representative of CH2M HILL will accept a groundwater sample immediately after collection by the PRP in a 1,000-ml plastic sample container. The container will be tagged with the sample number which identifies the sampling location and the date of sampling.

The sample container and tag will be placed in a 2-mil polyethylene bag. Tags should be positioned so they can be read through the bag.
Section 6
SAMPLING PLAN FOR SOIL

The PRP's Field Sampling Plan For Groundwater Studies (October, 1989), Section 5.5.3, describes the surface soil samples to be collected as a part of the PRP's Groundwater Study. Splits of the samples collected by the PRP will be obtained by CH2M HILL oversight personnel in the field.

6.1 SUMMARY OF PRP ACTIVITIES

The PRP will collect soil samples outside Pond 6's dike to the north and south of the eastern end of Pond 6. Figure 6-1 shows the location of these sampling sites. The sites for waste sampling by the PRP are also shown.

The samples will be collected using a hand auger or corer. The samples will be placed in 4-oz widemouth glass sample bottles with Teflon-lined black phenolic caps.

The reader is referred to the PRP's field sampling plan for a more detailed description of the field activities. The description in this section is not intended to provide detail sufficient for assessing PRP adherence to the approved SAP.

6.2 SAMPLE FREQUENCY

As directed by EPA Region III, CH2M HILL will collect splits of 3 of the samples collected by the PRP for analysis. Table 1-1 summarizes the splits of the soil samples that will be collected during the study. The sample collection procedures to be used by the PRP are described in the PRP's Field Sampling Plan For Groundwater Studies (October, 1989). The PRP soil samples to be split will be selected by CH2M HILL's oversight personnel. The split samples will be obtained in the field after sample collection by the PRP.

6.3 SAMPLE DESIGNATION

Each split sample will be assigned a unique sample identification number. The sample numbering system will be:
CH-Sxxxx-Dxxxxxx

where

CH is the designation for CH2M HILL split sample  
Sxxxx is the soil location number  
Dxxxxxx is the date of sampling.

This numbering scheme corresponds to the PRP’s numbering scheme with the exception of the CH prefix, which distinguishes the split sample from the PRP’s original half of the sample.

6.4 COORDINATION OF COLLECTION WITH PRP FIELD PERSONNEL

The interaction with the PRP field personnel to obtain splits of homogenized samples will be coordinated and pre-arranged through EPA Region III. It is assumed that the PRP will collect a sufficient volume of sample to allow a split to be taken.

After the sample to be split is collected and mixed by the PRP field personnel, the sample volume will be divided into two equal portions and a representative of CH2M HILL will accept a split of the homogenized sample in two 6-oz sample containers (one for methyl mercury and one for total mercury analysis). The container will be tagged with the sample number which identifies the sampling location and the date of sampling. The sample container and tag will be placed in a 2-mil polyethylene bag. Tags should be positioned so they can be read through the bag.

WDCR45/009.51
Section 7
SAMPLING PLAN FOR WASTE

The PRP's Field Sampling Plan For Groundwater Studies (October, 1989), Section 5.5.1, describes the waste samples to be collected as a part of the PRP's Groundwater Study. Splits of the samples collected by the PRP will be obtained by CH2M HILL oversight personnel in the field.

7.1 SUMMARY OF PRP ACTIVITIES

The PRP will collect waste samples from Ponds 5 and 6. Figure 6-1 shows the locations of these samples in addition to the location of soil samples to be collected by the PRP.

The samples will be collected using a hand auger or corer. The samples will be placed in 4-oz widemouth glass sample bottles with Teflon-lined black phenolic caps.

The reader is referred to the PRP's field sampling plan for a more detailed description of the field activities. The description in this section is not intended to provide detail sufficient for assessing PRP adherence to the approved SAP.

7.2 SAMPLE FREQUENCY

As directed by EPA Region III, CH2M HILL will collect splits of 2 of the samples collected by the PRP for analysis. Table 1-1 summarizes the splits of the waste samples that will be collected during the study. The sample collection procedures to be used by the PRP are described in the PRP's Field Sampling Plan For Groundwater Studies (October, 1989). The PRP waste samples to be split will be selected by CH2M HILL's oversight personnel. The split samples will be obtained in the field after sample collection by the PRP.

7.3 SAMPLE DESIGNATION

Each split sample will be assigned a unique sample identification number. The sample numbering system will be:

CH-Wxxxx-Dxxxxxxx
where

CH is the designation for CH2M HILL split sample
Wxxxx is the waste sample location number
Dxxxxxx is the date of sampling.

This numbering scheme corresponds to the PRP’s numbering scheme with the exception of the CH prefix, which distinguishes the split sample from the PRP’s original half of the sample.

7.4 COORDINATION OF COLLECTION WITH PRP FIELD PERSONNEL

The interaction with the PRP field personnel to obtain splits of homogenized samples will be coordinated and pre-arranged through EPA Region III. It is assumed that the PRP will collect a sufficient volume of sample to allow a split to be taken.

After the sample to be split is collected and mixed by the PRP field personnel, the sample volume will be divided in two equal portions and a representative of CH2M HILL will accept a split of the homogenized sample in two 6-oz sample containers (one for methyl mercury and one for total mercury analysis). The container will be tagged with the sample number which identifies the sampling location and the date of sampling. The sample container and tag will be placed in a 2-mil polyethylene bag. Tags should be positioned so they can be read through the bag.

WDCR45/013.51
Section 8
DOCUMENTATION AND SHIPPING REQUIREMENTS

For all samples collected, chain-of-custody protocols must be followed as well as specific shipping requirements. Coordination will be required with the oversight analytical laboratory. These procedures, as well as holding time and general recordkeeping requirements are described for all media in this section.

8.1 CHAIN-OF-CUSTODY RECORD

A CH2M HILL representative will assume custody of the sample container of the homogenized sample. As stated in A Compendium of Superfund Field Operations Methods, December 1987, a sample is under custody if:

- It is in the representative's possession
- It is in the representative's view, after being in the representative's possession
- It is in the representative's possession and then is placed in a secure area
- It is in a designated secure area.

For biological samples, it is anticipated that at the PRP laboratory, the CH2M HILL representative will assume custody of the sample container immediately prior to preparing the sample container for shipment.

For groundwater, soil, and waste samples, the CH2M HILL field oversight personnel will assume custody of the sample container immediately before preparing the sample container for shipment. Shipment will occur within 2 days of the date that the sample is collected. Shipment will occur on the same day that custody of the sample container is assumed.

The CH2M HILL representative will complete the COC record form, shown by Figure 8-1, using waterproof ink. Any corrections will be made by drawing a single line through the error and initialing and dating the correction. Information may not be erased or rendered unreadable.

The following information will be specified for each sample on the COC form:

AR300798
# Chain of Custody Record

## Environment Protection Agency
Region I Waste Management Division

<table>
<thead>
<tr>
<th>PROJECT NO.</th>
<th>PROJECT NAME</th>
<th>NO. OF CONTAINERS</th>
<th>REMARKS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
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</table>

**SAMPLERS:** (Signature)  

<table>
<thead>
<tr>
<th>STA NO</th>
<th>DATE</th>
<th>TIME</th>
<th>COMM.</th>
<th>STATION LOCATION</th>
<th>REMARKS</th>
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<th>Date / Time</th>
<th>Received by: (Signature)</th>
<th>Relinquished by: (Signature)</th>
<th>Date / Time</th>
<th>Received by: (Signature)</th>
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<tr>
<th>Relinquished by: (Signature)</th>
<th>Date / Time</th>
<th>Received for Laboratory by: (Signature)</th>
<th>Date / Time</th>
<th>Remarks</th>
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</tbody>
</table>

**Remarks:**  

**Distribution:** Original accompanies shipment; Copy to Coordinator Field Files

---

**Figure 8-1**  
CHAIN-OF-CUSTODY RECORD FORM  
Saltville Waste Disposal Site  
Saltville RI/FS Oversight
At the time of relinquishing the samples for shipment, the CH2M HILL representative will enter the following information on the COC form:

(6) His/her signature
(7) Date and time samples are relinquished
(8) Shipper's name
(9) Airbill number

Procedures for packing the coolers are described in Section 8.2, "Shipping Requirements." In terms of COC protocol, the following steps must also be taken:

- Enclose the top, original signature copy of the COC record form in plastic and secure it to the inside of the cooler lid.
- Secure the shipping coolers (fasten securely) and place custody seals across cooler openings. (Note that as long as custody forms are sealed inside the sample cooler and custody seals remain intact, commercial carriers are not required to sign off on the custody form.)
- The second copy of the COC record form will be retained by the CH2M HILL representative and the third copy will be retained and given to the Site Manager (SM).

Upon receipt of the coolers, the Oversight Analytical Laboratory will record the condition of the custody seals in the sample receipt logbook.

8.2 SHIPPING REQUIREMENTS

The bagged sample containers will be placed in an insulated cooler and surrounded by styrofoam or vermiculite packing materials for stability during transport. The cooler will be packed with sufficient dry ice or bagged ice to maintain an internal temperature of less than 4°C. Properly executed documentation (Section 2.3.1) must be sealed in a plastic bag and taped to the inside of the cooler lid. The cooler
will be secured with fiber tape and custody seals to maintain its integrity during shipment.

8.3 COORDINATION OF SHIPMENT WITH OVERSIGHT ANALYTICAL LABORATORY

The Oversight Analytical Laboratory will be notified by the CH2M HILL representative on the day that the shipment is sent. Upon receipt of the coolers, the Oversight Analytical Laboratory will record the condition of the custody seals in the sample receipt logbook.

8.4 HOLDING TIME

The holding time for total mercury in water according to available CLP SOWs is 28 days. A holding time of 28 days for methylmercury was selected on the basis of the holding time of total mercury in water samples. This same holding time is also given for total mercury in all other media and for methylmercury in all media for consistency. There is some concern about the volatility of methylmercury; thus, 28 days for the holding time was selected to minimize its loss from samples. The biological samples will be kept frozen until analysis. The groundwater, soil, and waste samples will be kept at a temperature of less than 4°C until analysis.

8.5 RECORDKEEPING

In addition to the COC record forms described under Section 8.1 above, the following record keeping documentation is required:

- Sample identification tags
- Sample identification labels
- Custody seals
- Packing lists
- SAS packing lists
- Shipping logs
- Inorganics traffic reports
- Field notebooks
- Photographs

8.5.1 Sample Identification

The sample tag is shown in Figure 8-2, and the sample label is shown in Figure 8-3. Sample tags will be secured to the containers of the split samples generated at the PRP laboratory. The sample tag should be filled out as follows:
Figure 8-2
SAMPLE IDENTIFICATION TAG
Saltville Waste Disposal Site
Saltville RI/FS Oversight
<table>
<thead>
<tr>
<th>SITE NAME</th>
<th>DATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANALYSIS</td>
<td>TIME</td>
</tr>
<tr>
<td></td>
<td>PRESERVATIVE</td>
</tr>
</tbody>
</table>

C 82421931

SPECIALTY CLEANED CONTAINER

Figure 8-3
SAMPLE IDENTIFICATION LABEL
Saltville Waste Disposal Site
Saltville RI/FS Oversight
Project Code—Enter the number assigned by EPA to the sampling project.

Station No.—Enter the unique CH2M HILL sample identification number ("CH" + PRP Sample No.) used to document that sample. (See Section 2.2.)

Month/Day/Year—Enter the six-digit number indicating the month, day, and year that the sample was collected in the field.

Time—Enter the time (military) the sample was collected in the field.

Designate: Comp. or Grab—Check the appropriate box to indicate whether the sample is a composite or a grab sample.

Station Location—Enter the sampling station from which the sample was collected.

Analyses—Check the appropriate box for the analysis "mercury" for total mercury analysis or enter "methylmercury" in the blank at the bottom of the list and check the corresponding box for methylmercury analysis.

Remarks—Note the date and time that the CH2M HILL representative assumed custody of the split sample in the PRP laboratory.

Samplers (Signatures)—The CH2M HILL representative will sign the sample tag after filling in all of the required information.

In addition to the sample tags, adhesive labels must be attached to each container and marked in indelible ink with the CH2M HILL sample number. The labels are to be covered with clear waterproof tape.

8.5.2 Custody Seals

After the samples, packing material, coolant (ice or dry ice), packing list, and COC record form are placed in the insulated cooler, the cooler must be sealed with custody seals (Figure 8-4). At least two seals must be placed on each shipping cooler, one each on the front and back, in such a manner that if the cooler were opened the seal would
Figure 8-4
CUSTODY SEAL
Saltville Waste Disposal Site
Saltville RI/FS Oversight
be broken. Clear tape will be placed over the seals to reduce the chance that the seals may be accidentally broken during shipment.

Upon receipt of containers in the Oversight Analytical Laboratory, custody seals are to be inspected and the condition recorded.

8.5.3 Packing List

The packing list (shown in Figure 8-5) must be completed for samples shipped to the Oversight Analytical Laboratory. The packing list describes the samples shipped in each cooler. The Oversight Analytical Laboratory will verify that the samples listed on the packing list are in the cooler for each shipment received at the laboratory.

8.5.4 Special Analytical Service (SAS) Packing List

The SAS packing list shown in Figure 8-6 must be completed for samples shipped to the CLP laboratory. This packing list describes the samples shipped in each cooler. The CLP laboratory will verify the condition of each sample for each shipment received at the laboratory.

8.5.5 Shipping Log

A shipping log (See Figure 8-7) must be completed to document the samples shipped and to identify QC samples. The shipping log is not sent to the analytical laboratory. (QC samples are to be blind to the laboratory.) The field oversight personnel will copy the shipping log and send the original shipping log to the Field Coordinator after each sampling episode.

8.5.6 Inorganics Traffic Report

The traffic report, shown in Figure 8-8, is a four-part carbonless form to be shipped with samples to the CLP laboratory. Traffic reports document case number, site name, laboratory performing the analysis, samplers, names, sample label number, analytical parameters, and sample matrix.

The inorganic traffic reports will be used for samples to be analyzed for SAS parameters (total mercury) by a CLP laboratory. The bottom two pages of the traffic report will be
1. CH2M HILL Sample Collector:
   Name:
   Phone:

2. CH2M HILL Field Coordinator NELLINE SCHEUER
   Phone: (703) 471-1441
   Airbill No.:

<table>
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<tr>
<th>(A) Sample Number</th>
<th>(B) Sample Description (From Box 5)</th>
<th>(C) Homogenized (Y or N)</th>
<th>(D) Date/Time Homogenized</th>
<th>(E) Conc. (L=low M=med H=high)</th>
<th>(F) Analysis</th>
<th>(G) Special Handling</th>
<th>(H) Sample Station</th>
<th>(I) Sample Condition On Receipt at Laboratory</th>
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</tbody>
</table>

5. Sample Description: (Enter in Column B)
   1. Surface Water
   2. Groundwater
   3. Rinse
   4. Soil/Sediment/Waste
   5. Other (Specify)
U.S. ENVIRONMENTAL PROTECTION AGENCY  
CLP Sample Management Office  
P.O. Box 818 - Alexandria, Virginia 22313  
Phone: 703/557-2490 - FTS/557-2490

SPECIAL ANALYTICAL SERVICE  
PACKING LIST

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<th>Sampling Date(s):</th>
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<th>For Lab Use Only</th>
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<th>Sample Condition on Receipt at Lab</th>
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</tbody>
</table>

For Lab Use Only

White - SMO Copy, Yellow - Region Copy, Pink - Lab Copy for return to SMO, Gold - Lab Copy

Figure 8-6  
SAS PACKING LIST  
Saltville Waste Disposal Site  
Saltville RI/FS Oversight
## Sample Shipping Log

### CH2M HILL Sample Collector:

1. **Name**

2. **Phone**

### CH2M HILL Field Coordinator: NELLIE SCHEUER

Phone: (703) 471-1441

### Ship To:

3. **Attention:**

4. **Phone:**

### Sample Description:

- Surface Water
- Groundwater
- Rinse
- Soil/Sediment/Waste
- Other (Specify)

### Sample Data

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Designate QC Sample</th>
<th>Sample Description (From Box 4)</th>
<th>Total Mercury</th>
<th>Methyl Mercury</th>
<th>Sample Packing List No.</th>
<th>Lab Name</th>
<th>Date Shipped</th>
<th>Total Mercury</th>
<th>Methyl Mercury</th>
</tr>
</thead>
<tbody>
<tr>
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</tbody>
</table>

### Notes:

- CH2M HILL Sample Collector's Copy (Send to Field Coordinator After Each Sampling Episode)
- CH2M HILL Sample Manager

**Figure 8-7**

Saltville RI/FS Oversight
### United States Environmental Protection Agency

#### Inorganic Traffic Report

**For CLP Use Only**

<table>
<thead>
<tr>
<th>Field</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sample Description</td>
<td>Enter in Column A</td>
</tr>
<tr>
<td>2. Region Number</td>
<td></td>
</tr>
<tr>
<td>3. Sampling Co.</td>
<td></td>
</tr>
<tr>
<td>4. Date Shipped</td>
<td>Airbill Number</td>
</tr>
<tr>
<td>5. Date Received</td>
<td>Received by</td>
</tr>
<tr>
<td>6. Laboratory Contract Number</td>
<td>Unit Price</td>
</tr>
<tr>
<td>7. Transfer to</td>
<td>Date Received</td>
</tr>
<tr>
<td>8. Contract Number</td>
<td>Price</td>
</tr>
<tr>
<td>9. Strict Conc.</td>
<td>Phases (Check below)</td>
</tr>
</tbody>
</table>

#### CLP Sample Number

<table>
<thead>
<tr>
<th>CLP Sample Number</th>
<th>(A) Sample Description</th>
<th>(B) Concentration</th>
<th>(C) RAS Analysis</th>
<th>(D) Special Handling</th>
<th>(E) Station Location</th>
<th>(F) Date/Time of Sample Collection</th>
<th>(G) Corresponding Organic Sample Number</th>
<th>(H) Sample Condition on Receipt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(From box 5)</td>
<td>H=low</td>
<td>Total Metals</td>
<td>Cyanide</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

#### Notes

- Double volume required for matrix split/duplicate aqueous sample.
- Ship medium and high concentration samples in paint cans.
- See reverse for additional instructions.

---

**Figure 8-8**

**INORGANICS TRAFFIC REPORT**

Saltville Waste Disposal Site

Saltville RI/FS Oversight
shipped with the samples to the CLP laboratory, and the top two copies will be retained by the sampler. These copies will be kept in the site files.

8.5.7 Field Notebooks

Field notebooks will be used to record general data collection activities performed by the PRP at the site. Entries will be in waterproof ink and written in sufficient detail so that a history of the sampling event can be reconstructed with minimum reliance on memory.

Field notebooks to be used will be bound field survey books. Notebooks will be assigned to field oversight personnel.

After project completion these documents will be in the custody of the Field Coordinator. Each notebook will be identified by the project-specific number. Pages will be numbered.

The cover of the notebook will indicate:

- Person or organization to whom book is assigned
- Book number
- Project name
- Start date
- End date

Notebook entries will contain a variety of information. At the beginning of each daily entry the field oversight personnel will record the date, start time, and current weather. The oversight personnel will record the names of field personnel present, the level of personal protection being used onsite, the names of visitors to the site, and the purpose of their visit. Difficulties, accidents, incidents, or deviations from the work plan will be recorded and explained in the notebook. The bottom of each page will be signed by the person making entries. Each line on a page should be used or, if not used, should be crossed out, signed, and dated.

In addition to a general description of the overall data collection activities, the oversight personnel will record any deviations by the PRP personnel in sample/data collection from the PRP's SAP. Unusual or notable measurements will also be recorded. The person making entries will initial the entries. Corrections will be made by drawing a single line through the error and initializing and dating the correction. Information may not be erased or rendered
unreadable. Wherever sample/data collection is recorded in the oversight field notebook, a detailed description of the location of the station will be recorded.

Equipment used by oversight personnel to make measurements will be identified along with the date of last calibration. Any equipment used by oversight personnel to collect samples will also be noted, along with the time of sampling and all field parameters measured.

8.5.8 Photographs

Photographs of selected sampling and other field work will be taken on a regular basis. A data-back-equipped camera will be used. The picture number and roll number (if more than one roll of film is used) will be logged in the field notebook to identify which sampling location is depicted in the photograph.

The first frame on each roll will identify the roll by containing an information sign. The project and film roll number should be written on the sign to identify the sampling episode activities and sampling locations. For example:

Saltville RI/FS Oversight
Roll Number 1
January 15, 1990
Soil Sampling
NFHR Station No. 1

Subsequent photographs will include an identifying object in the background. No filter or special lenses other than a UV filter will be used. The serial number of the 35-mm camera body will be entered in the logbook.
Section 9
REFERENCES


Health and Safety Plan
I. GENERAL INFORMATION

CLIENT: EPA-Region III  JOB NO: WDC63107.PP.WP
PROJECT MANAGER: Sadia Kissoon/WDC
SITE NAME: Saltville
SITE LOCATION: Saltville, Virginia
PURPOSE OF FIELD VISIT(S): Provide oversight of PRP RI activities.
DATE OF VISIT(S): March 1990
BACKGROUND INFORMATION: Complete Preliminary X
INFORMATION AVAILABLE FROM: WDC (office)
OVERALL HAZARD SUMMARY: Serious Moderate Low X Unknown

II. SITE CHARACTERISTICS

FACILITY DESCRIPTION (site map attached)

During the period from 1951 to 1972, Olin Company operated an electrolytic chlorine and caustic soda plant at the Saltville Site. One of the electrodes used in the chlorine-caustic process contained mercury, which was released into the process wastes and onto the plant grounds. Waste Pond 5 was used to dispose of waste sludges from the chlor-alkali processes. In 1963, Waste Pond 6 was constructed to receive overflow from Waste Pond 5. No wastes containing mercury were supposedly dumped into Waste Pond 6, but structural components of the old chlor-alkali plant reportedly were buried at the eastern edge of the pond.

At present, the Saltville Site includes the former chlor-alkali plant area and the two surface impoundments termed Waste Ponds 5 and 6. Offsite areas include approximately 80 miles of the North Fork of the Holston River (NFHR) beginning at the Saltville Site and continuing downstream to Weber City, Virginia.

The former chlor-alkali plant area is currently fully capped and vegetated. The site is fenced on three sides, but is somewhat accessible by crossing the river or by walking across a railroad bridge southwest of the site. A small residential area of approximately 50 homes is located between the former chlor-alkali plant and Waste Pond 5. The site layout map is shown in the attached map. (Risk Assessment, Saltville Waste Disposal Site, September, 1986.)

Features and Unusual Features (water supply, telephone, radio, power lines, gas lines, watermains, terrain, etc.): Site borders the North Fork of the Holston River as shown on site map.

Status (active, inactive, unknown): Inactive. PRP's are presently remediating the site.

History (worker or non-worker injury; complaints from public; previous agency action): Sampling of air, soils, surface water, sediments and biota from the NFHR has been performed during the past 15 years, with mercury being detected in all media. Air monitoring has detected insignificant levels of particulate mercury; however, elevated mercury vapor concentrations were detected in June 1983, while remedial activities were being conducted at the site. Surface water sampling by ORNL in 1975 detected insignificant levels ($0.2 \mu g/l$) of dissolved mercury in filtered water, but significant ($1 \text{ ppm}$) levels of mercury on suspended particulates in the river. Mercury in the Waste Pond 5 effluent ranged from 10 to 120 $\mu g/l$. Low levels of cadmium, lead, and arsenic ($\leq 10 \mu g/l$) were also found in Waste Pond 5 effluent. The results of waste sampling and analysis led to the conclusion that about 53,000 lb of mercury are contained in Waste Pond 5 with 92 percent (49,000 lb) contained in the upper 17-1/2 feet. The mercury is concentrated in the west end, the northeast corner, and the far east end of the pond. Mercury in the upper 17-1/2 feet of these area (29 acres total) represents about 69 percent of the total mercury in the pond. Sediment sampling in the NFHR showed that significant levels (above 1 ppm) are present at most stations up to 80 river miles downstream from the Saltville site. The majority of fish samples collected below the Saltville site contained edible-portion mercury concentrations greater than 1.0 ppm (Risk Assessment, Saltville Waste Disposal Site, September, 1986).

III. WASTE CHARACTERISTICS

WASTE TYPE(S)

Liquid ___ Solid ___ Sludge ___ Gas ___

CHARACTERISTIC(S)

Corrosive ___ Ignitable ___ Radioactive ___

Volatile ___ Toxic ___ Reactive ___ Unknown ___ Other (Name) ___
IV. HAZARD EVALUATION

**Overall Hazard Level:** The overall hazard level posed to personnel during oversight activities is low to moderate. The major hazard is inhalation exposure to mercury vapor and dermal contact from inorganic and organic (methyl) mercury contaminated soils and groundwater. Since waste pond #s contains most of the mercury onsite (53,000 pounds), drilling and sampling activities within the pond, and at its perimeter, poses the greatest mercury vapor exposure hazard to oversight personnel. The remaining area of the site poses a minimal mercury exposure and contact hazard since the plant area has been fully capped with clean fill.

Since estimates of the percentage of methyl mercury comprising the total mercury onsite is in question, personnel protection procedures will be designed to provide protection against methyl mercury. Methyl mercury presents a greater hazard to personnel than does inorganic mercury because it is more toxic and is not efficiently adsorbed by air-purifying respirators. As a result, Level B protection is the only mean for protecting personnel against the inhalation hazards of methyl mercury.

Oversight activities will not involve actual sampling and well installation tasks. These tasks will only be observed by oversight personnel with mercury vapor air monitoring equipment used at the immediate work area to identify the mercury vapor exposure hazard. Mercury vapor concentrations detected in the work area greater than its TLV (0.01 mg/m³ for a sustained period (10 minutes) will require oversight personnel to evacuate the immediate work area until mercury vapor levels less than 0.01 mg/m³ are observed. Should this procedure become infeasible for oversight activities, Level B protection will be required and implemental onsite. This will cause oversight activities to stop until the provisions for Level B protections are made and this SSP is amended, accordingly.

**Chemical Hazards:** Inorganic and organic mercury emits vapors that are toxic by inhalation and skin absorption. The TLV for inorganic mercury is 0.05 mg/m³ while the TLV for organic mercury is 0.01 mg/m³ for an 8-hour time weighted average (TWA) exposure. Symptoms of acute over-exposures include coughing, chest pains, bronchitis, headache, irritation of the eyes and skin. Chronic over-exposures to mercury cause central nervous system (CNS) and kidney disorders. The CNS effects are manifested by tremors, insomnia, irritability, fatigue, and weakness. Other clinical effects include gastrointestinal disturbances, anorexia, and weight loss.

**Physical Hazards:**

Cold stress can be a hazard. If temperatures are below freezing or if it is raining, schedule a 10 minute warm-up break every 2 hours in a heated
area. Remove or open clothing to prevent overheating during the breaks. Drink at least 8 oz of non-alcoholic, non-caffeinated beverage during each break. Soup or hot chocolate would be best. Take a 30 minute lunch break not later than 5 hours after startup. Observe team members for frostbite or severe shivering. Both of these conditions require an immediate warm-up break. Wear multi-layer clothing under Tyvek to protect against the cold.

Noise levels greater than 90 dbA may be present in the immediate drilling area. Should shouted conversation become difficult to interpret at a distance of 6 inches, hearing protection must be worn. Personnel may keep a sufficient distance from drilling operations to prevent the need for hearing protection. Should hearing protection be worn, earmuffs attached to hard hats are preferred over ear inserts or plugs to minimize potential contamination of the inner ear.

**Hazards Posed by Site Activities**

Drilling poses safety hazards to personnel in the immediate vicinity of the drill rig. To protect personnel from overhead falling objects (i.e., bolts, wrenches, pieces of pipe), hard hats must be worn in the immediate vicinity of the drilling. Safety glasses are also required to protect against flying projectiles that could be caused by hammering fittings/connections and driving retaining clips. Although drilling activities near overhead electrical lines is not anticipated, the driller shall maintain a distance of 20 feet from the drill rig mast to all overhead electrical lines. The driller is responsible for safety around the drill rig during drilling activities. The CH2M HILL observer must comply with the driller's safety precautions and should remain outside the immediate work zone of an active drill rig.

**V. PROCEDURES**

**SITE ORGANIZATION**

Map/Sketch Attached  X  Site Secured  X  
Perimeter Identified  X  Zone(s) of Contamination Identified  X  

4  
AR300818
SITE PERSONNEL

Team Organization:

<table>
<thead>
<tr>
<th>Team Member</th>
<th>Responsibility</th>
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<tbody>
<tr>
<td>Brian McDonald/ATL</td>
<td>Observer</td>
</tr>
<tr>
<td>Dawn Saunders/DFB</td>
<td>Observer, SCC for CH2M HILL only</td>
</tr>
<tr>
<td>Keith Roberts/Olin</td>
<td>Buddy for CH2M HILL observer</td>
</tr>
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</table>

(K. Roberts is not covered by this plan, but must receive a copy of it and a briefing on the emergency provisions contained)

a--No record of CPR training

Each of the team members named above meets the training and medical surveillance requirements of 29CFR1910.120. In addition, each is currently certified by the American Red Cross, or equivalent, in both first aid and CPR.

Note: The SSC is to complete Form 533 (attached) and return it to Mary Anne Chillingworth/WDC at the end of each week.

Level of Protection:

A _____ B _____ C _____ D X

Level D: Steel toe, steel shank neoprene boots; safety glasses; regular Tyvek coveralls; inner latex gloves and outer neoprene gloves; tape gloves and boots to Tyvek; wear hard hat in the immediate drilling work areas.

Safety Equipment and Materials: First aid kit. Eye wash with backup clean water for a 15 minute eye wash.

Monitoring Equipment and Procedures: Inspect and read the instruction manual for the Jerome Mercury Vapor Analyzer before using in the field. Calibrate before each day's activity according to the manufacturer's instruction. Record calibration in the log book. Monitor oversight personnel's breathing zone continuously during intensive site activities. Record readings above background every 30 minutes. Notify plan approver of any difficulties encountered during operation of the instrument.
Action Level: (Breathing Zone)

Background to .01 mg/m³ mercury vapor—Level D

Greater than .01 mg/m³ mercury vapor for 10 minutes—evacuate immediate work area until readings less than .01 mg/m³ are observed on the instrument.

Note: Should these procedures become infeasible, Level B protection will be required. As a result, oversight activities would cease until Level B was implemented onsite. This SSP needs to be amended for Level B protection.

SITE ENTRY PROCEDURES

- Locate nearest available telephone.
- Confirm and post emergency telephone numbers and route to hospital.
- Designate at least one vehicle for emergency use.
- Meet with designated buddy and review this plan.

WORK LIMITATIONS (Time of day, etc.)

- Daylight hours only.
- No eating, drinking or smoking onsite.
- No contact lenses onsite.
- Buddy system at all times on site within the exclusion zone.
- CH2M HILL employees to wear TLD badge at all times when on or near the site.
- Practice contaminant avoidance.

DECONTAMINATION PROCEDURES

Personnel: Wash, rinse, and remove outer gloves and booties; remove Tyvek; remove inner gloves; wash hands and face before eating; shower as soon as practical after leaving the site; coordinate decontamination procedures with PRPs.
DISPOSAL OF MATERIALS GENERATED ON SITE

Place disposable PPE onsite at PRP facilities.

VI. CONTINGENCY PLAN

If an injury occurs, take the following steps:

- Prevent further injury and notify SSC.
- Initiate first aid and get medical attention for the injured immediately. (Coordinate emergency procedures with PRP's contractor).
- Depending upon the type and severity of the injury, call the medical consultant and/or occupational physician.
- Notify the Health and Safety Manager.
- Notify the injured person's personnel office.
- Prepare an incident report. The SSC is responsible for ensuring its preparation and submittal to the Health and Safety Director and CH2M HILL corporate personnel office within 48 hours.
- The SSC will assume charge during a medical emergency.

LOCAL (CH2M HILL Form 311, Emergency Phone Numbers, to be posted)

All Emergency Services: 703/783-7204

Police Department: 703/496-4321

Fire: 703/496-7113

Paramedic: 703/783-7204 (Marin)

Hospital: 703/783-3141 (Smyth County Community Hospital)
          703/783-2032 (ER)

EMERGENCY ROUTES (completed in the field with map attached to plan)
EMERGENCY CONTACTS

• CH2M HILL Medical Consultant
  Name: Dr. Kenneth Chase, Washington Occupational Health Associates, Inc.
  Phone: 202/463-6698 (8-5 EST)
        202/463-6440 (after hours answering service; physician will return call within 30 minutes)

• CH2M HILL Federal Programs Health and Safety Manager
  Name: Mike Adams/ORO
  Phone: 615/483-9032(O)

• Occupational Physician
  Name: Dr. Prater
  Phone: 404/455-7008

  Team members under his care:
  Brian McDonald
  Name: Dr. Anesta
  Phone: 305/278-3323

  Team members under his care:
  Dawn Saunders

• CH2M HILL Project Manager
  Name: Sadia Kissoon/WDC
  Phone: 703/471-1441

• Client Contact
  Name: Paul Leonard
  Phone: 215/597-1286

• CH2M HILL ARC III Program Regional Manager
  Name: Robert Dagostaro
  Phone: 703/471-1441
• CH2M HILL Personnel Office

Name: Beth Sexton
Phone: 703/471-1441

If an injury occurs, notify the injured person’s personnel office as soon as possible after obtaining medical attention for the injured. Notification MUST be made within 24 hours of the injury.

• CH2M HILL Director of Health and Safety

Name: David Lincoln/SEA (Acting)
Phone: 206/453-5000
Address: CH2M HILL
P.O. Box 91500
Bellevue, WA 98009-2050

• CH2M HILL Corporate Personnel Office

Name: Sharon Robinson/CVO
Phone: 503/752-4271
Address: CH2M HILL
2300 N.W. Walnut Blvd.
Corvallis, OR 97330

VII. PLAN APPROVAL

This site safety plan has been written for the use of CH2M HILL, its employees and subcontractors. CH2M HILL claims no responsibility for its use by others. The plan is written for the specific site conditions, purposes, dates and personnel specified and must be amended if these conditions change.

PLAN PREPARED BY: Nelline K. Scheuer Date: 11/15/88
APPROVED BY: Angelo Liberatore Date: 11/23/88
AMENDED/APPROVED BY: Angelo Liberatore Date: 1/9/89
AMENDED/APPROVED BY: MaryAnne Chillingworth Date: 3/5/90
Attachments:

- Site Map
- Form 311, Emergency Phone Numbers
- Form 533, Record of Hazardous Waste Field Activity

Distribution of approved plan:

Site manager (responsible for distribution of team members and client) Health and Safety Manager

WDCHS3/088.50
<table>
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<tr>
<th>Service</th>
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<th>Address</th>
<th>Contact</th>
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<tr>
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<td>Owner</td>
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<td>ATTN:</td>
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This notice is located at: ________________________________

WDHS3/088.50
FORM 533

RECORD OF HAZARDOUS WASTE FIELD ACTIVITY

SITE NAME:
SITE SAFETY COORDINATOR:
PROJECT NUMBER:
RECORD OF ACTIVITIES FOR (DATES):

<table>
<thead>
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<th>Employee Name</th>
<th>Total Days</th>
<th>Days at the Site in</th>
<th>Number of days as SSC</th>
<th>Activities Employees Performed</th>
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<tr>
<td></td>
<td>Days Onsite</td>
<td>Level B  Level C  Level D</td>
<td>Level B  Level C  Level D</td>
<td>While Onsite</td>
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Signature of SSC: ____________________________

WDHS3/088.50

AR300826