November 13, 2009

Mr. Sam Chummar
Work Assignment Manager
U.S. Environmental Protection Agency (EPA)
77 W. Jackson Blvd. (SR-6J)
Chicago, IL 60604

Subject: **Sampling and Analysis Plan (SAP) for the Plainwell Mill Site, Operable Unit No. 7 of Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site Plainwell, Kalamazoo County, Michigan Remedial Action Contract (RAC) 2 No. EP-S5-06-02 Work Assignment No. 041-RSBD-059B**

Dear Mr. Chummar:

SulTRAC is submitting the electronic copy of the sampling and analysis plan (SAP) for the above-referenced project. The SAP consists of the field sampling plan (FSP) and the quality assurance project plan (QAPP). In addition, SulTRAC will deliver two hard copies and two electronic copies of the draft SAP on compact disc to you, as requested in EPA's statement of work for the Plainwell Mill site issued to SulTRAC.

If you have any questions regarding this submittal, please call me at (312) 201-7491.

Sincerely,

Jeffrey J. Lifka
SulTRAC Project Manager

Enclosure

cc: Norvelle Merrill-Crawford, EPA Contracting Officer (letter only)
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UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY

"...TO PROTECT HUMAN HEALTH AND SAFEGUARD THE NATURAL ENVIRONMENT..."

**REMEDIAL ACTION CONTRACT 2
FOR REMEDIAL, ENFORCEMENT OVERSIGHT,
AND NONTIME-CRITICAL REMOVAL ACTIVITIES IN REGION 5**

SAMPLING AND ANALYSIS PLAN (SAP) FOR THE PLAINWELL MILL SITE, OPERABLE UNIT NO. 7 OF ALLIED PAPER, INC./PORTAGE CREEK/ KALAMAZOO RIVER SUPERFUND SITE

PLAINWELL, KALAMAZOO COUNTY, MICHIGAN

**November 13, 2009
Work Assignment: 041-RSBD-059B
Contract Number: EP-S5-06-02**

**Prepared for
U.S. Environmental Protection Agency
Region 5
Chicago, IL**

Prepared by:

ST SulTRAC

SAMPLING AND ANALYSIS PLAN
PLAINWELL MILL SITE, OPERABLE UNIT NO. 7 OF
ALLIED PAPER, INC./PORTAGE CREEK/KALAMAZOO RIVER SUPERFUND SITE
PLAINWELL, KALAMAZOO COUNTY, MICHIGAN

SulTRAC has prepared this Remedial Investigation/Feasibility Study (RI/FS) sampling and analysis plan (SAP) for the Plainwell Mill Site, Operable Unit No. 7 of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund (Plainwell Mill Site) in Plainwell, Michigan, under the U.S. Environmental Protection Agency (EPA) Remedial Action Contract (RAC) 2 for Region 5, Contract No. EP-S5-06-02, Work Assignment (WA) No. 041-RSBD-059B. The draft SAP discusses RI/FS oversight activities that SulTRAC will perform consisting of two tasks: (1) split sampling and (2) general oversight. RI/FS oversight requested by EPA for Phase II activities is scheduled to begin in November 2009. The RI/FS includes possible soil, sediment, groundwater, and/or surface water sampling in order to further characterize the nature and extent of contamination at the Plainwell Mill Site.

As requested in EPA's statement of work (SOW) for the site, SulTRAC has prepared this SAP in two parts: the field sampling plan (FSP) is provided in Attachment A, and the quality assurance project plan (QAPP) is provided in Attachment B. These plans are among the site-specific plans to be prepared under the WA in accordance with Task 1 of the EPA SOW.

REMEDIAL ACTION CONTRACT 2
FOR REMEDIAL, ENFORCEMENT OVERSIGHT, AND
NON-TIME CRITICAL REMOVAL ACTIVITIES
IN REGION 5

ATTACHMENT A

FIELD SAMPLING PLAN
FOR PLAINWELL MILL, OPERABLE UNIT NO. 7 OF THE ALLIED PAPER, INC. /PORTAGE CREEK/KALAMAZOO RIVER SUPERFUND SITE PLAINWELL, KALAMAZOO COUNTY, MICHIGAN

Prepared for
United States Environmental Protection Agency
Region 5
77 West Jackson Boulevard
Chicago, IL 60604

Work Assignment No.	:	041-RSBD-059B
EPA Region	:	5
Date Prepared	:	November 13, 2009
Contract No.	:	EP-S5-06-02
Prepared by	:	SulTRAC
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ACRONYMS AND ABBREVIATIONS

AST	Aboveground storage tank
BBL	Blasland, Bouck & Lee
°C	Degrees Celsius
CD	Consent decree
CLP	Contract Laboratory Program
COC	Chain of custody
CRA	Conestoga-Rovers & Associates, Inc.
CRL	Central Regional Laboratory
EPA	U.S. Environmental Protection Agency
ERM	Environmental Resource Management
FS	Feasibility study
FSP	Field sampling plan
FTC&H	Fisbeck, Thompson, Carr & Huber
FTL	Field team leader
HASP	Health and safety plan
HAZWOPER	OSHA 40-hour Hazardous Waste and Emergency Response Certification
HCL	Hydrochloric Acid
HNO_3	Nitric Acid
ID	Identification
IDW	Investigation-derived waste
MCL	Maximum contaminant level
MDEQ	Michigan Department of Environmental Quality
mL	Milliliter
MS	Matrix spike
MSD	Matrix spike duplicate
NA	Not Applicable
OU	Operable unit

PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PPE	Personal protective equipment
PRP	Potentially responsible party
PTFE	Polytetrafluoroethylene
PVOC	Petroleum-related volatile organic compound
QA	Quality assurance
QAPP	Quality assurance project plan
QC	Quality control
RAC	Remedial Action Contract
RI	Remedial investigation
RMT	RMT, Inc.
ROD	Record of Decision
SAP	Sampling and analysis plan
SARA	Superfund Amendments and Reauthorization Act
SPLP	Synthetic precipitation leaching procedure
SMO	Sample Management Office
SOW	Statement of work
SVOC	Semivolatile organic compound
TAL	Target analyte list
Taplin	Taplin Environmental Services, Inc.
TriMatrix	TriMatrix Laboratories, Inc.
TSCA	Toxic Substances Control Act
UST	Underground storage tank
VOC	Volatile organic compound
WA	Work assignment
WAM	Work assignment manager
Weyerhaeuser	Weyerhaeuser Company

1.0 INTRODUCTION

SulTRAC has prepared this field sampling plan (FSP) in partial fulfillment of the requirements of the U.S. Environmental Protection Agency (EPA) statement of work (SOW) (EPA 2008) for Work Assignment (WA) No. 041-RSBD-059B under Remedial Action Contract (RAC) 2 No. EP-S5-06-02 for Region 5. SulTRAC has prepared this FSP as part of the sampling and analysis plan (SAP) for Plainwell Mill, operable unit (OU) No. 7 of the Allied Paper/Portage Creek/Kalamazoo River site in Kalamazoo County, Michigan. The SAP consists of this FSP (Attachment A) and the quality assurance project plan (QAPP) (Attachment B), which are among the site-specific plans to be prepared under the WA in accordance with Task 1 of the EPA SOW (EPA 2008). Quality assurance (QA) and quality control (QC) protocols associated with sampling and analysis are presented in the QAPP. This FSP describes sampling activities to be conducted by SulTRAC during (1) split sampling events and (2) oversight of potentially responsible party (PRP) field investigations conducted by Conestoga-Rovers & Associates, Inc. (CRA). CRA is the consultant performing the work on behalf of Weyerhaeuser Company (Weyerhaeuser), the PRP for the site.

SulTRAC will perform field oversight of the PRP during the remedial investigation (RI)/feasibility study (FS). The goal of the RI/FS is to obtain the minimum amount of data necessary to support selection of an approach for site remediation, and then to use these data to support a Record of Decision (ROD). The goals of field oversight activities are to (1) verify that CRA conducts field work in accordance with EPA-approved project plans and (2) collect split samples for independent laboratory analysis. Split samples collected by SulTRAC will be analyzed through EPA's Contract Laboratory Program (CLP); however, in order to match the PRP's project-specific quantitation limits, split samples to be analyzed for metals will be analyzed through a commercial laboratory subcontracted directly to SulTRAC.

In 2009, CRA was retained by Weyerhaeuser to perform the Phase II RI. This FSP was prepared using information presented in the Multi-Area FSP and Multi-Area QAPP prepared by RMT Inc., (RMT) (RMT 2008a, b), and the Multi-Area QAPP and Multi-Area FSP amendments prepared by CRA on behalf of Weyerhaeuser (CRA 2009a, b). This FSP discusses anticipated oversight activities, based on discussions with the EPA work assignment manager (WAM), and proposed field activities presented in the latest revision (September 2009) of the Phase II RI work plan prepared by CRA (CRA 2009c).

2.0 SITE DESCRIPTION AND HISTORY

The Plainwell Paper Mill, OU No. 7 (the site), is an approximately 34-acre parcel located at 200 Allegan Street, Plainwell, Allegan County, Michigan. The property is occupied by (1) the now vacant Plainwell Paper Mill, (2) wastewater treatment structures associated with paper manufacturing, and (3) the vacant Specialty Minerals, Inc. property. The site is currently owned by the City of Plainwell, which is discussing plans for its re-use to include utilizing the property for a new town hall and other mixed-use facilities. The site is bordered by the Kalamazoo River to the north, Mill Race and commercial properties to the east, Allegan Street (M-89) to the south with mixed residential/commercial buildings beyond this, and residential properties and the City of Plainwell Sewage Treatment Facility to the west.

2.1 SITE HISTORY

The site had been the location of papermaking operations for over 100 years beginning in 1884 at the earliest and ending in 2000 with the closing of the facility. The original footprint of the mill and the site itself had increased since inception of operations through 1995, when the Simpson Plainwell Paper Company purchased the final addition. Ownership of the property changed several times throughout the history of the site, ending in 2000 with the bankruptcy of the Simpson Plainwell Paper Company. In 2006, the site was acquired by the City of Plainwell. Weyerhaeuser, which owned the facility between 1961 and 1970, is the current PRP for the site. Weyerhaeuser was identified as a PRP for the Allied Paper site in a General Notice letter dated April 8, 2004, received by Weyerhaeuser and two other PRPs (RMT 2008a). Concurrently, Weyerhaeuser was negotiating a Consent Decree (CD) to undertake specific activities on the former Plainwell Mill and 12th Street Landfill sites. On February 22, 2005, Weyerhaeuser entered into a CD with the EPA for the Design and Implementation of Certain Response Activities at the 12th Street Landfill site (OU No. 4) and the Plainwell Mill site (OU No. 7). During Weyerhaeuser's period of ownership, lagoons previously constructed on site were used for dewatering sludge during wastewater treatment. The excavated sludge was disposed of at the 12th Street Landfill. Polychlorinated biphenyls (PCB) were released from ink involved in manufacturing and recycling carbonless copy paper from 1954 to 1971. PCBs were banned by the Toxic Substances Control Act (TSCA), enacted by Congress in 1976 and implemented in 1977.

In addition to activities conducted on site that potentially generated PCBs, coal was stored and used during operations, parts-cleaning solvents were used, and tanks containing petroleum products were

necessary for operations. As a result, in addition to PCBs, other possible contaminants at the site are volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH), and metals.

In 2009, Weyerhaeuser changed project coordinators from RMT to CRA. Subsequently, CRA submitted to EPA for review amendments to the Multi-Area QAPP and Multi-Area FSP (CRA 2009a, b), and a revised Phase II RI work plan (CRA 2009c).

The site location is shown on Figure 1.

2.2 FORMER SITE INVESTIGATIONS

Previous investigations at the site have been performed in three areas of the Plainwell Mill site: (1) the former wastewater sludge dewatering lagoon and aeration basin area; (2) the north-central portion of the site, including the former coal pile storage area and the vicinity of the No. 6 fuel oil tank; and (3) the mill buildings area (RMT 2008b). Remedial actions and confirmation sampling were also performed in response to a spill near the No. 6 fuel oil tank, to elevated PCB concentrations found in a storm sewer and a former wastewater discharge pipe located on the northern side of the mill buildings, and during an Emergency Action to remove paper residuals from along the Mill Banks. One of the investigations was conducted by Blasland, Bouck & Lee (BBL), as part of the EPA-approved RI for the Allied Paper, Inc./ Portage Creek/Kalamazoo River Superfund site. For the purpose of due diligence for a prospective property transfer, other investigations were conducted by consultants to the Simpson Plainwell Paper Company, or by previous and current owners. The information was provided to the Michigan Department of Environmental Quality (MDEQ) as part of the State's baseline environmental assessment process.

Former Wastewater Sludge Dewatering Lagoon and Aeration Basin Area

Three investigations have occurred in this area, including soil sampling as part of the EPA-approved remedial investigation for the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund site and soil and groundwater sampling as part Phase II Environmental Site Assessments performed by Environmental Resource Management (ERM) in 1997 and by Fishbeck, Thompson, Carr & Huber (FTC&H) in 2006. The primary objective of the BBL investigation was to assess whether the Plainwell Mill may have been a potential source of PCBs to the Kalamazoo River. To achieve this objective, Geoprobe® borings were advanced in 11 of the 14 former wastewater sludge dewatering lagoons and in the former aeration basin (see Figure 2). For the investigation by ERM in 1997, the primary objectives were to determine the

concentrations of metals in soil and whether contaminants present in the lagoons had adversely affected groundwater. As part of the study, shallow groundwater samples were collected from temporary wells at two locations, along with soil samples from Lagoons I, J, M, and N (see Figure 2). In 2006, FTC&H advanced four borings and installed one shallow temporary groundwater monitoring well to verify or eliminate previously cited recognized environmental conditions in this area.

North Central Portion of the Site

Three investigations have occurred in this area of the site, including a geotechnical investigation in 1980, a Phase II Environmental Site Assessment by ERM in 1996, and post-excavation soil sampling by Taplin Environmental Services, Inc., (Taplin) and Plainwell Paper Company in 1999. The objective of the geotechnical investigation by Wilkins & Wheaton in 1980 was to visually characterize the soil located in the vicinity of the then-proposed building addition. The scope of the investigation included installing 20 soil borings. For the Phase II environmental assessment by ERM in 1996, the objective was to determine if constituents of potential concern were present in three areas in the north-central portion of the site: (1) the 200,000-gallon fuel oil aboveground storage tank (AST) area, (2) the former coal pile storage area, and (3) the area located between the former coal pile storage area and the Kalamazoo River. The scope of the ERM investigation included collection and analysis of soil and groundwater samples. Finally, following a fuel oil spill in 1999, Taplin and Plainwell Paper Company collected confirmatory samples in an area adjacent to the No. 6 fuel oil containment structure. As part of the cleanup of the spill, Taplin had removed free liquids, contaminated soil, and absorbents from the area. The scope of post-excavation soil sampling included collection of samples for analyses for petroleum-related volatile organic compounds (PVOC) and PAHs.

Mill Buildings Area

Previous investigations in this area of the site included sampling and analysis of soil in areas near former wastewater treatment operations, and of sediment contained in a storm sewer and a former wastewater discharge pipe in 1994; sampling and analysis of soil and groundwater as part of a Phase II Environmental Site Assessment performed in 1996 and 2006; and sampling of soil on the Plainwell Mill site for PCB analysis, as part of a larger investigation that focused on bank soil in the Kalamazoo River. Remediation of PCB-containing sediment in the storm sewer and former wastewater discharge pipe was also performed. The primary objectives of the BBL investigation were to determine if elevated levels of PCBs were present in soil in the area of the former primary clarifier, a possible wastewater sludge storage

area, and a potential warehouse construction area; and in sediment in a storm sewer and in a former wastewater discharge pipe. The sample collected from inside the storm sewer manhole was also analyzed for dioxin congeners. For the assessment performed by ERM in 1996, the objectives were to determine if constituents of potential concern were present in the soil near the former 300-gallon gasoline underground storage tank (UST), or in the groundwater downgradient of the former gasoline UST, kerosene UST, or diesel AST─all formerly located along the northern side of the mill buildings. The assessment by FTC&H in 2006 included groundwater sampling near the No. 6 fuel oil AST and downgradient of the AST/UST area near the mill buildings.

In a letter to Weyerhaeuser dated February 19, 2008, EPA requested additional work along the former Plainwell Mill banks (RMT 2008a), in response to discovery of elevated concentrations of PCBs and oily soil encountered along the Plainwell Mill banks during the separate Plainwell Mill Banks Emergency Response activities. In 2008, RMT dug a series of test pits along the Plainwell Mill banks. RMT also installed 12 monitoring wells and three staff gauges at the site in conducting an initial assessment of groundwater conditions. The results of RMT's 2008 sampling activities were reported to EPA in February 2009 (RMT 2009).

A preliminary list was developed of chemicals of interest potentially at concentrations hazardous to human health and the environment at the Plainwell Mill site. These chemicals of interest had been identified via previous investigations of the soil and groundwater, previous site operations, and information obtained by SulTRAC. At a minimum, semivolatile organic compounds (SVOC), metals, and PCBs are present at the site. Specific contaminants detected (in soil or groundwater) include the following:

- Antimony
- Arsenic
- Benzo(a)pyrene
- Cadmium
- Copper
- Cyanide
- Dibenxo(a,h)anthracene
- Lead
- Mercury
- PCBs
- Phenanthrene

CRA is currently Weyerhaeuser's consultant, and has submitted a revised work plan for the Phase II investigation (CRA 2009c), revised QAPP (CRA 2009a), and a revised field sampling plan (CRA 2009b). CRA's plans are currently pending EPA approval as of the preparation date of SulTRAC's SAP for EPA. All PRP and SulTRAC plans are expected to be approved prior to mobilization to the site in late November or early December 2009 for the Phase II investigation intended to further characterize the soil, groundwater, sediment, and surface water at the site.

3.0 PROJECT OBJECTIVE

This FSP describes the approach for conducting all PRP oversight and split sampling activities. The goals of field oversight activities are to (1) verify that CRA conducts field work in accordance with EPA-approved project plans and (2) collect split samples for independent laboratory analysis. The PRP will collect samples from soil, sediment, surface water, and groundwater. As directed by EPA, SulTRAC will split about 25 percent of the samples collected by the PRP (an estimated 80 soil and 10 groundwater samples). All field work is to proceed in accordance with procedures specified in the PRP's updated project plans.

4.0 FIELD SAMPLING ACTIVITY

SulTRAC has been tasked to provide oversight of PRP sampling efforts. Split samples collected by SulTRAC (estimated as approximately 80 soil and 10 groundwater samples) will be analyzed for VOCs, SVOCs, PCBs, and metals (including mercury and cyanide). In addition, SulTRAC will collect soil samples for synthetic precipitation leaching procedure (SPLP) metals analysis and will request the laboratory to hold these samples for possible further analysis pending total metals analytical results. As part of this sampling effort, SulTRAC will also collect QA/QC samples. Field duplicates will be collected at a frequency of one for every 10 samples collected. Matrix spike and matrix spike duplicate (MS/MSD) samples will be collected at a frequency of one for every 20 samples collected. One trip blank will accompany every VOC shipment sent to the laboratory.

SulTRAC's knowledge of the site is based on published site investigations and assessments. Furthermore, the scope of Phase II RI sampling activities is specified in the FSP and QAPP amendments and Phase II RI work plan prepared by CRA. Therefore, final decisions regarding actual sampling depths and locations are based on the most recent site-related documents as approved by EPA.

Possibly, after final sampling locations have been approved by EPA, some changes may occur at the discretion of the PRP's field team leader (FTL) based on field conditions. Any changes will be documented by SulTRAC oversight personnel. Because SulTRAC will be conducting oversight of PRP sampling activities, the locations and depths of split samples collected by SulTRAC is dictated by the locations and depths of samples collected by the PRP. SulTRAC oversight personnel will use their discretion to select split sample locations and depths. Reasons for selecting particular sampling locations may include the presence of staining, odors, visible product, and the desire to collect samples from various media and locations throughout the site. Assumedly, all proposed sampling locations will be accessible, except for one confined space (the coal tunnel) that SulTRAC personnel will not access in accordance with the SulTRAC health and safety plan (SulTRAC 2009).

Although the Phase II RI work plan presents the proposed sampling locations, the exact number and locations of samples to be collected by the PRP is somewhat flexible pending field observations. The following subsections describe the different areas and matrices that SulTRAC anticipates sampling at the Plainwell Mill Site as part of the PRP oversight field activities.

4.1 SOIL

SulTRAC will collect split soil samples from the site area as part of the PRP oversight. During the RI/FS oversight, SulTRAC will collect split samples at approximately 25 percent of the PRP sampling locations. This percentage is an approximation and provides an indication of EPA's general intent and desired level of oversight. The PRP plans to collect soil samples from soil borings and test pits on site. Of these soil samples, the PRP proposes to have all soil samples analyzed for VOCs, SVOCs, metals including cyanide, and PCBs. In addition, the PRP will collect soil samples for SPLP metals analysis and may direct its laboratory to hold these samples for possible further analysis pending total metals analytical results. Therefore, all soil split samples collected by SulTRAC will be analyzed for VOCs, SVOCs, metals including cyanide, and PCBs, and SulTRAC will follow the same protocol for collecting and possibly analyzing soil samples for SPLP metals.

4.2 GROUNDWATER

The PRP will conduct groundwater sampling from the entire monitoring well network after additional monitoring wells are installed, as well as during vertical aquifer testing to occur at two locations. SulTRAC will collect split groundwater samples from the monitoring wells and during vertical aquifer testing as part of the PRP oversight. SulTRAC will collect split samples at approximately 25 percent of the PRP groundwater sampling locations. This percentage is an approximation, and provides an indication of EPA's general intent and desired level of oversight. The PRP proposes to have all groundwater samples (monitoring well and vertical aquifer testing samples) analyzed for VOCs, SVOCs, metals (plus low level mercury, methyl mercury, and cyanide), and PCBs. Therefore, all groundwater split samples collected by SulTRAC will be analyzed for VOCs, SVOCs, metals (plus low level mercury and cyanide), and PCBs. As discussed with the EPA WAM, SulTRAC will not request the lab to analyze groundwater split samples for methyl mercury.

5.0 FIELD SAMPLING PROCEDURES

The general field sampling procedures to be used by the PRP are specified in the Multi-Area FSP and QAPP amendments (CRA 2009a, b) and the Phase II RI work plan (CRA 2009c). This section describes the general procedures for SulTRAC's collection of split samples.

5.1 SOIL SAMPLING PROCEDURES

Soil samples from various locations and depths to be determined in the field will be collected at the site. SulTRAC oversight personnel will use their discretion to select split sample locations and depths. Reasons for selecting particular sampling locations may include the presence of staining, odors, visible product, and the desire to collect samples from various locations and depths in order to obtain split samples representative of the entire site.

Split sample collection procedures will likely include one of the following methods:

- SulTRAC personnel will hand the sample containers to CRA personnel and they will fill the containers accordingly.
- SulTRAC personnel will collect samples side-by-side with CRA at a given location.

5.2 GROUNDWATER SAMPLING PROCEDURES

Groundwater samples will be collected from various locations across the site. SulTRAC oversight personnel will use their discretion to select split sample locations and depths. Reasons for selecting particular sampling locations may include the presence of staining, odors, visible product, and the desire to collect samples from various locations and depths in order to obtain split samples representative of the entire site.

Split sample collection procedures will likely include one of the following methods:

- SulTRAC personnel will hand the sample containers to CRA personnel and they will fill the containers accordingly.
- SulTRAC personnel will collect samples side-by-side with CRA at a given location.

In either case, sample aliquots for each analysis should be collected at the same time. For example, the PRP's personnel would fill their containers for VOCs, and then SulTRAC personnel would fill their containers for VOCs. This sequence is to be followed for SVOCs, PCBs, and metals.

6.0 LABORATORY ANALYTICAL METHODS

Table 1 presents the laboratory methods for analyzing the samples collected by SulTRAC. The majority of split samples will be analyzed by a CLP laboratory. Soil and groundwater split samples to be analyzed for metals (including low-level mercury and cyanide) will be analyzed by a commercial laboratory subcontracted directly to SulTRAC in order to meet the reporting limits specified in CRA's QAPP (CRA 2009a). SulTRAC has selected TriMatrix Laboratories, Inc., (Tri Matrix) to perform the metals analyses for soil and groundwater split samples.

TABLE 1
ANALYTICAL METHODS SUMMARY

Parameter	CLP Analytical Method	Tri Matrix Analytical Method
Soil		
VOCs	CLP SOW SOM01.2	--
SVOCs	CLP SOW SOM01.2	--
PCBs	CLP SOW SOM01.2	--
TAL metals	--	SW-846 Method 6010B/6020A
Mercury	--	SW-846 Method 7471A
Cyanide	--	SW-846 Method 9010B/9014
SPLP metals	--	Extraction by SW-846 Method 1312; analysis by SW-846 Method 6010B/6020A
SPLP mercury	--	Extraction by SW-846 Method 1312; analysis by SW-846 Method 7470A
SPLP cyanide	--	Extraction by SW-846 Method 1312; analysis by SW-846 Method 9014
Groundwater		
VOCs	CLP SOW SOM01.2	--
SVOCs	CLP SOW SOM01.2	--
PCBs	CLP SOW SOM01.2	--
TAL metals	--	SW-846 Method 6020
Mercury	--	SW-846 Method 1631E
Cyanide	--	SW-846 Method 9014

Notes:

CLP	Contract Laboratory Program
PCB	Polychlorinated biphenyl
SOW	Statement of work
SOM01.2	Superfund Analytical Services/CLP, Multi-Media, Multi-Concentration Organic Analysis , EPA 2005
SPLP	Synthetic precipitation leaching procedure
SVOC	Semivolatile organic compound
VOC	Volatile organic compound
TAL	Target Analyte List

7.0 DECONTAMINATION PROCEDURES

SulTRAC will be collecting only split samples from the PRP; therefore, all decontamination of field supplies and equipment will be conducted by the PRP.

8.0 SAMPLE HANDLING PROCEDURES

SulTRAC will collect split samples of soil and groundwater, prepare the samples for shipment, and complete all necessary documentation. Sample containers, preservatives, holding times (see Table 2), identification, documentation, chain of custody, packaging, and shipping are discussed in this section.

8.1 SAMPLE CONTAINER, PRESERVATION, AND HOLDING TIMES

Table 2 lists sample containers, preservation requirements, and holding times for the sampling to occur in the field.

8.2 SAMPLE IDENTIFICATION

SulTRAC will follow the PRP's sample identification scheme as described in Section 3.1 of the PRP's FSP (CRA 2009b); however, SulTRAC will add an "S" to the beginning of the sample number to identify it as a split sample on its subcontractor laboratory's (TriMatrix Laboratories) chain-of-custody (COC) form.

For samples sent to a CLP laboratory, each sample will also be assigned an identifying number by CLP Forms-II Lite software. Forms-II Lite was developed to expedite sample documentation, track samples from the field to the laboratory, and reduce the most common documentation issues associated with sampling. The user will enter information on the site, project, sampling team, analysis, location, matrix, collection time and date, and sample and tag numbers before or during the sample event.

TABLE 2
SAMPLE CONTAINER, PRESERVATION, AND HOLDING TIMES

Matrix	Analyte	Sample Container[1]	Preservation Requirements[1]	Maximum Holding Time[2]
Soil	VOCs[1]	Three 40-mL glass containers (containing 10 grams of soil per vial) with PTFE-lined septa and open tip screw caps, reweighed and containing magnetic stir bars and one 2-ounce container of sample filled with no headspace for determination of moisture content -OR- at least three coring tools used as transport devices (e.g., 5-g samplers) and one container of sample for determination of moisture content.	Preserved with 10 mL of methanol and iced to 4 ± 2ºC immediately	48 hours (frozen) to preservation at laboratory for analysis following preservation 14 days from sample collection
Soil	SVOCs	One 4-ounce, wide-mouth glass jar	Cool to 4 ±2°C immediately after collection	14 days/40 days
Soil	PCBs	One 4–ounce, wide-mouth glass jar	Cool to 4 ± 2°C immediately	14 days/40 days
Soil	Metals, Mercury, and Cyanide	One 16–ounce, wide-mouth glass jar (extra volume: 8-ounces required for synthetic precipitate leaching procedure for cyanide and mercury)	Cool to 4 (± 2°C) immediately	6 months Metals 28 days Mercury 14 days Cyanide
Water	VOCs	Three 40-mL glass vials with PTFE-lined septa and open top screw caps	No headspace, Cool to 4 ± 2°C, adjust pH to less than 2 with HCl	NA/14 days
Water	SVOCs	Two 1-liter amber glass bottles fitted with PTFE-lined screw caps	Cool to 4 ±2°C immediately after collection	7 days/40 days
Water	PCBs	Two 1-liter amber glass bottles, fitted with PTFE-lined screw caps	Cool to 4 ± 2°C immediately	7 days/40 days
Water	Metals	One 500–mL , high-density polyethylene bottle with polyethylene-lined caps	Acidify to pH <2 with HNO_3 and cool to 4 ± 2°C immediately	6 months
Water	Cyanide	One 500–mL, high-density polyethylene bottle with polyethylene-lined caps	Preserve to pH > 12 with NaOH and cool to to 4 ± 2°C immediately	14 days
Water	Low-level mercury	Two 40-mL glass vials with PTFE-lined septa and open top screw caps	No headspace, no cooling or HCL preservation in field required, BrCl is added at laboratory	28 days (sample is oxidized in sample container at laboratory)

Notes:

BrCl Bromine chloride
°C Degrees Celsius
HCl Hydrochloric Acid
NA Not applicable
NaOH Sodium Hydroxide
PRP Potentially responsible party
HNO_3 Nitric Acid
PCB Polychlorinated biphenyl
PTFE Polytetrafluoroethylene
SVOC Semivolatile organic compound
VOC Volatile organic compound
mL Milliliter

[1] Actual VOC sample collection and preservation methods will be verified with the PRP prior to start-up of field work.
[2] Holding time is measured from time of sample collection to the time of sample extraction and analysis (EPA 2004).

8.3 SAMPLE LABELS

Forms-II Lite generates labels for each sample to be submitted to a CLP laboratory. A sample label will be affixed to all sample containers. The label will be completed with the following information:

- Project number
- CLP case number
- CLP sample number
- Sample station name (the sample identification [ID] discussed above)
- Sample collection date and time
- Preservative
- Sample collector's initials
- Analysis
- Sample tag number.

After labeling, if required, each sample will be will be preserved as required (see Table 2). For samples sent to TriMatrix, SulTRAC will use laboratory-provided sample labels.

8.4 SAMPLE DOCUMENTATION

Sampling will be documented in a logbook using indelible ink. The header of each page will include the site location name, date, and project number. At the start of each day, the weather, site condition, field staff present, subcontractors present, and any conducted safety meeting or other, shall be noted. The collection time, sample identification number (not CLP ID), sample depth (if appropriate), sample location description, field observations, sampler's name, and time of sample collection will be recorded in the logbook for each and every sample. Every MS/MSD and duplicate should also be clearly designated in the field logbook. Preparation of trip blanks will be documented with applicable parameters in the same manner as described above. The sample identification, location, and time will be recorded in the field log book.

Each page of the logbook will be dated, numbered (if appropriate), and signed at the bottom by SulTRAC personnel. Any residual space on the last page of each day's log book will be crossed out with a single line. Each new sampling day will begin on a new page in the log book. Any corrections made during the same day of sampling should be crossed out with one single line, or the term "backnote" can be inserted to account for missed time.

The field team leader ensures that all documentation in the logbook is done appropriately and according to the procedure described above, and should check this documentation daily. Any corrections or additions can be made on a subsequent page with appropriate documentation, although this procedure is not recommended. Corrections or additions are best made on the same day as sampling.

All field logbooks must be kept secure at all times by the field team leader while conducting field work. As possible, all field log books shall be scanned electronically at high resolution, minimum 300 by 300 DPI. If electronic scans cannot be conducted after 1 week of continuous field work, high-resolution hardcopies must be made and kept secure until the logbooks can be scanned. All completed field books and any hardcopies will be stored with the project manager. Field data records will be maintained in accordance with Multi-Media Investigation Manual and Procedures (EPA 1992) and SulTRAC's FSP.

8.5 SAMPLE CHAIN OF CUSTODY

SulTRAC will use standard sample custody procedures to maintain and document sample integrity during collection, transportation, storage, and analysis in accordance with the SulTRAC RAC II Contract Level QAPP. A sample will be considered in custody if one of the following statements applies:

- It is in a person's physical possession or view.
- It is in a secure area with restricted access.
- It is placed in a container and secured with an official seal such that the sample cannot be accessed without breaking the seal.

Forms-II Lite generates and prints COC forms, called traffic reports, in Forms II Lite (a laboratory copy and a region copy). The laboratory copy will be sealed inside the lid of the cooler. COC procedures provide an accurate written record that traces possession of individual samples from the time of collection in the field to the time of acceptance at the laboratory. One COC record will be generated for each cooler shipped. The COC record also will be used to document all samples collected and analyses requested. The following information will be documented on the COC form:

- Project name and number (region copy only)
- CLP case number
- CLP sample numbers
- Sample tag numbers
- Sampling location (station identification)
- Name and signature of sampler
- Destination of samples (laboratory name)
- Sample ID number
- Date and time of collection

- Number and type of containers filled
- Analysis requested
- Preservatives used (if applicable)
- Sample designation (grab or composite)
- Special instructions (e.g., laboratory needs to sub-sample oversized material or perform additional homogenization)
- Signatures of all samplers
- Signatures of individuals involved in custody transfer, including the date and time of transfer
- Airbill number (if applicable)
- Project contact and phone number
- Custody seal number.

For samples sent to TriMatrix, SulTRAC will use laboratory-provided sample labels and COC forms which typically contain most of the information listed above.

SulTRAC will follow the procedures in the EPA Region 5 CRL *Superfund Amendments and Reauthorization Act (SARA)/Superfund Sample Handling Manual* (EPA 1989) to complete the documentation listed above.

SulTRAC will appoint one of its field technical staff members to serve as the sample custodian. When all required documents have been completed, the sample custodian will sign and date the document and list the time of the sample collection. The custodian will also confirm that all descriptive information is complete on the COC forms, which will be included with each shipping container. Two custody seals total will be used: one with the custody seal placed across the latch of the container, and the other affixed on the opposite side of the container lid. The lid will be securely taped shut for shipment. For samples being sent to the CLP laboratory, the field sample custodian will send the original copies of the COC region copy to the project manager, who in turn will submit these forms to the Region 5 Sample Management Office (SMO), care of Warren Layne, within 5 working days. The sample custodian will also retain and scan all copies of all COCs (laboratory and region) for the project files.

8.6 SAMPLE PACKING AND SHIPPING

The following procedures will be implemented when samples collected during this project are shipped:

- All samples jars will be individually wrapped with bubble wrap or other packing material and placed in their own individual Ziploc-type bags. For samples going to a CLP laboratory, the CLP ID tag for each sample will accompany the sample package.
- Ice will be double bagged in large Ziploc-type bags and placed at the bottom of the cooler. If the cooler has a drain, it will be taped shut both inside and outside of the cooler.

- The cooler will be lined with bubble wrap or other packing material, and all individually packaged samples will be placed into one large plastic bag and tied after all sample jars have been input. Sufficient packing material will be used to prevent sample containers from breaking during shipment.
- Additional ice, double bagged, will be added on top of the tied plastic bag full of samples. Enough ice will be added to maintain a sample temperature of 4 ± 2 degrees Celsius (°C). SulTRAC will prepare, label, and place a temperature blank in each cooler.
- The laboratory should be notified if a sampler suspects that any sample contains anomalously high or low concentrations (handwrite this anomaly directly on the laboratory copy of the COC), or if handling a sampled substance requires laboratory personnel to take safety precautions.
- The COC specific to each cooler will be sealed inside a plastic bag and taped to the inside of the cooler lid. Ensure that the COC is signed by all samplers and the custody seal numbers are included on the COC. For samples going to a CLP laboratory, include with the COC a return pre-paid air bill so the cooler may be returned to SulTRAC.
- The cooler will be closed and taped shut with strapping tape around both ends.
- Signed and dated custody seals will be placed on the front and side of each cooler. Wide clear tape will be placed over the seals to prevent accidental tearing.
- The air bill, if required, will be completed before the samples are relinquished to the carrier.
- The COC will be transported within the taped sealed cooler. When the cooler is received at the analytical laboratory, laboratory personnel will open the cooler and sign the COCs to document transfer of samples.
- For samples going to a CLP laboratory, the Superfund SMO will be notified if the laboratory should expect to receive samples on a Saturday. SulTRAC should call its CLP sample coordinator, who in turn will notify the SMO.

All shipping containers will be labeled as required by the U.S. Department of Transportation. After packaging, the samples will be shipped to the CLP laboratory specified by the EPA Region 5 Regional Sample Control Coordinator or to TriMatrix, as appropriate.

9.0 DISPOSAL OF INVESTIGATION-DERIVED WASTE

Investigation derived waste (IDW) is waste generated from an activity related to split sampling at the site. IDW can include solid and hazardous waste, media (including soil, sediments, groundwater, and surface water), and debris that contain "listed" hazardous waste or that exhibit a characteristic of a hazardous waste. IDW can include media and debris that are not hazardous, but contaminated with hazardous constituents.

During sampling activities, IDW will be generated by the PRP. Disposable, single use materials and equipment used for decontamination will be disposed of properly. Personal protective equipment (PPE), tools, buckets, brushes, and all other contaminated equipment must be secured in drums or other containers, and labeled as described in Section 6.0 of the Multi-Area FSP (CRA 2009b).

Additional IDW generated by SulTRAC, such as disposable PPE will be disposed of according to the same procedures specified in the Multi-Area FSP.

10.0 HEALTH AND SAFETY PROCEDURES

All field activities will be conducted in accordance with the SulTRAC Health and Safety Plan (HASP), which is among the site-specific plans prepared for the WA (SulTRAC 2009). Prior to initiation of field activities, all SulTRAC field personnel and subcontractors will read and sign the HASP, indicating that they understand the plan and agree to operate in accordance with its requirements. SulTRAC may operate under the PRP's HASP when providing oversight of the PRP's activities. All SulTRAC personnel and subcontractors must have 40-hour hazardous waste and emergency response (HAZWOPER) training, and proof of certification must be filed with the signed HASP. A complete copy of the site-specific plans, including the HASP, will be maintained by the field sampling team at the site.

11.0 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

All QA activities will be conducted in accordance with the SAP. A copy of the SAP will be maintained by the field sampling team for immediate use in resolving any QA issues that might arise during field activities.

QC samples will be collected at the following frequencies:

- Field Duplicate: One per 10 environmental samples will be collected, with a minimum of one per sample matrix.
- Trip Blank Samples: One trip blank will be included in each cooler containing samples for analysis for VOCs.
- MS/MSD Samples: One per 20 environmental samples per matrix will be collected.

Field duplicate samples consist of two separate samples collected from the same sampling location and depth, using the same equipment and sampling procedures. A trip blank is a clean sample of a matrix that is taken from the laboratory to the sampling site and transported back to the laboratory, without having been exposed to sampling procedures (typically analyzed only for volatile compounds). This sample is not to be labeled or identified as a trip blank for the CLP laboratory. Equipment rinsate blanks will not be collected by SulTRAC because this is a split sampling event. MS/MSD is an environmental sample divided into two separate aliquots, each of which is spiked with known concentrations of target aliquots. The two spiked aliquots, in addition to an unspiked sample aliquot, are analyzed separately, and the results are compared to determine the effects of the matrix on the precision and accuracy of the analysis. For groundwater samples, the MS/MSD generally requires collecting triple sample volume (three sets of vials), while for solid matrices, the MS/MSD does not require extra volume collection. All samples designated as MS/MSDs should be identified as “MS/MSD” for the CLP and Tri Matrix laboratories.

12.0 REFERENCES

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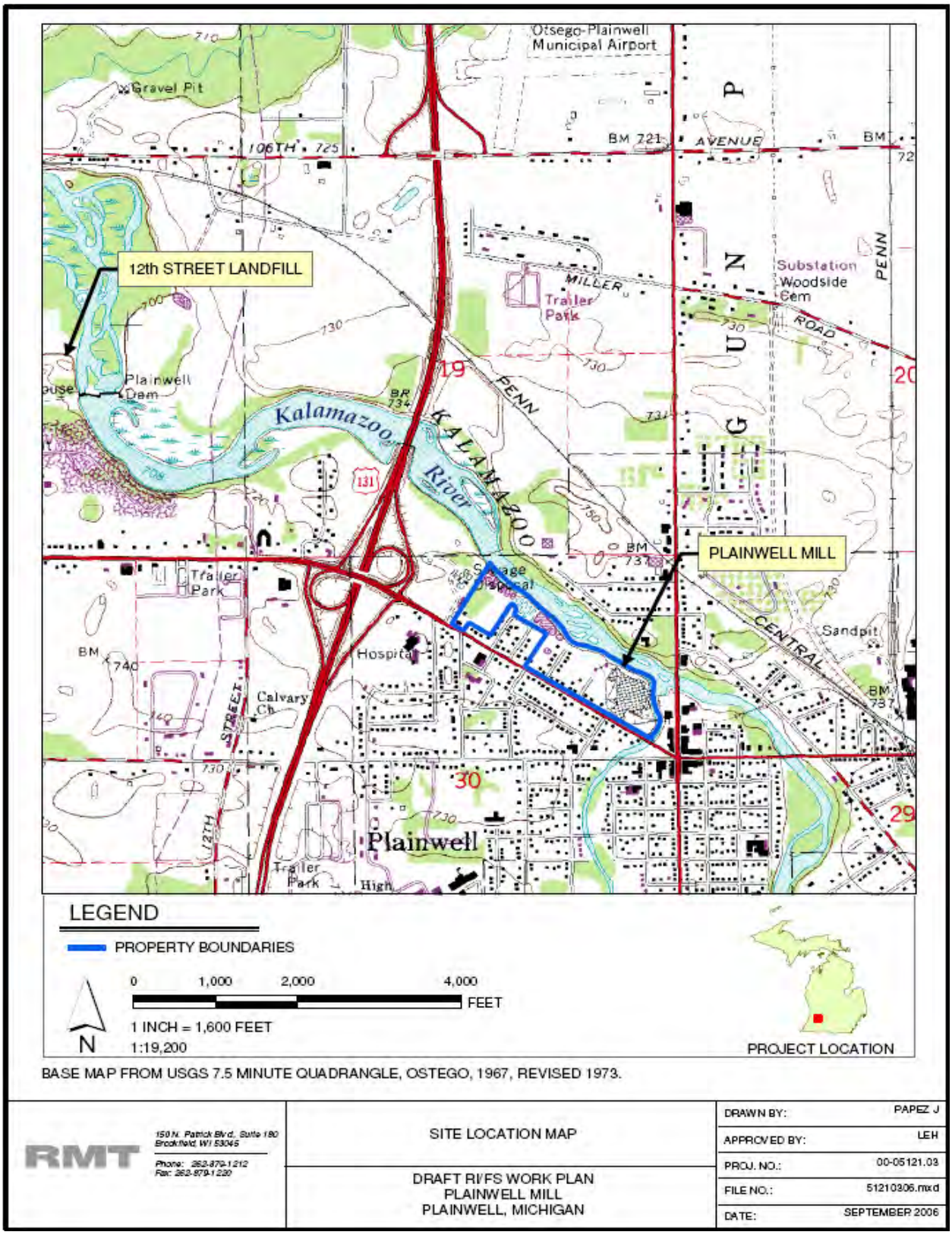
FIGURES

(Two Sheets)

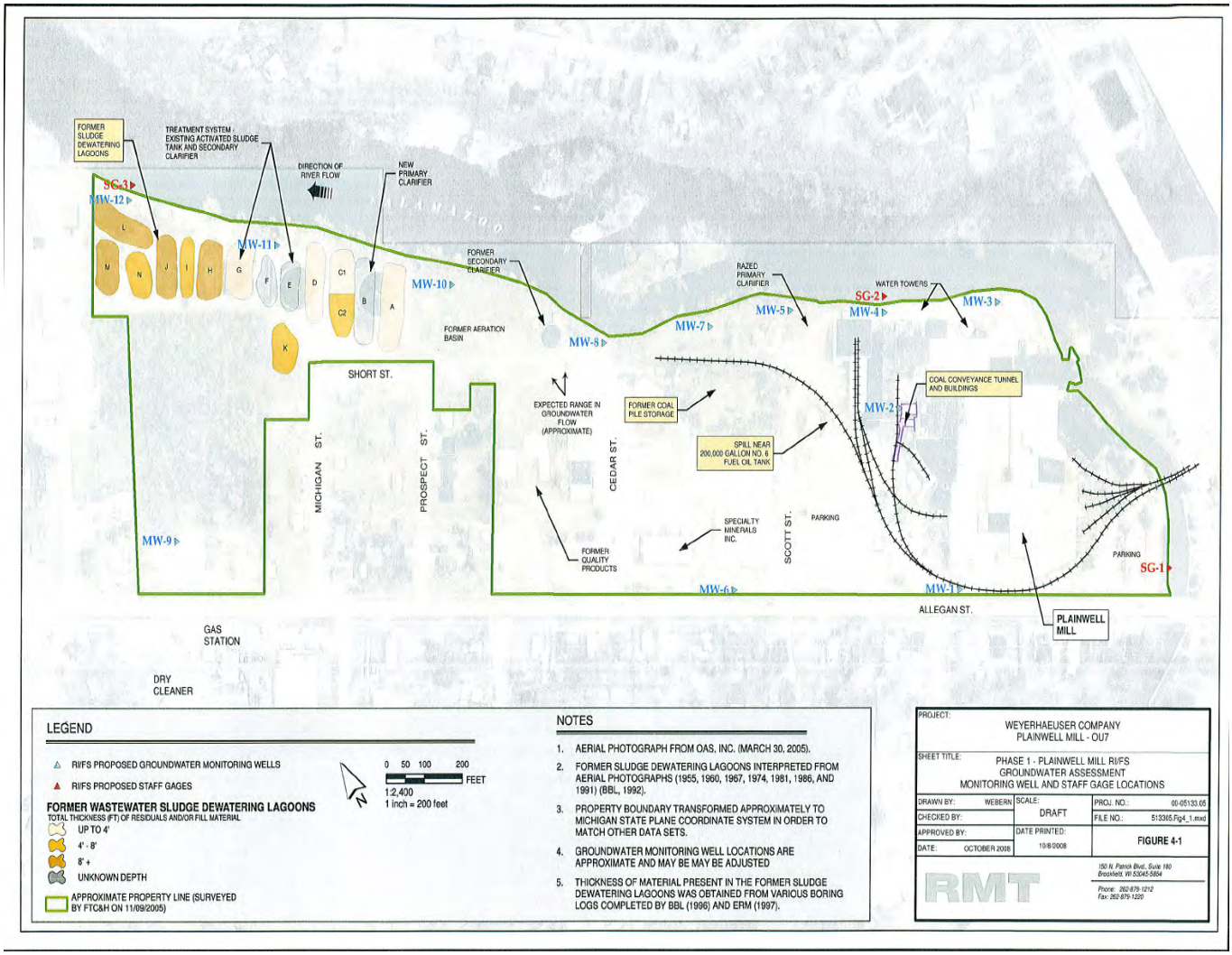
FIGURE 1
SITE LOCATION



BASE MAP FROM USGS 7.5 MINUTE QUADRANGLE, OSTEGO, 1967, REVISED 1973.

RMT 150 N. Patrick Blvd., Suite 190 Brookfield, WI 53045 Phone: 262-879-1212 Fax: 262-879-1220	SITE LOCATION MAP	DRAWN BY: PAPEZ J
		APPROVED BY: LEH
	DRAFT RI/FS WORK PLAN PLAINWELL MILL PLAINWELL, MICHIGAN	PROJ. NO.: 00-05121.03
		FILE NO.: 51210906.mxd
		DATE: SEPTEMBER 2006

FIGURE 2
SITE LAYOUT



Source for Figures 1 and 2:

Modified from RMT, Inc. 2008. "Initial Groundwater and Underground Coal Tunnel Assessment: Operable Unit 7 of the Allied Paper, Inc. / Portage Creek/Kalamazoo River Superfund Site." October.

REMEDIAL ACTION CONTRACT 2 FOR
REMEDIAL, ENFORCEMENT OVERSIGHT, AND
NON-TIME-CRITICAL REMOVAL ACTIVITIES
IN REGION 5

ATTACHMENT B

QUALITY ASSURANCE PROJECT PLAN FOR REMEDIAL INVESTIGATION/FEASIBILITY STUDY OVERSIGHT, PLAINWELL MILL, PLAINWELL, KALAMAZOO COUNTY, MICHIGAN

Prepared for
U.S. Environmental Protection Agency
Region 5
77 West Jackson Boulevard
Chicago, IL 60604

Date Submitted:	November 13, 2009
EPA Region:	5
Work Assignment No:	041-RSBD-059B
Contract No:	EP-S5-06-02
Prepared by:	SulTRAC
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APPENDIX A

TriMatrix Laboratories, Inc. Standard Operating Procedures

- GR-18-109_REV 3.3(10-10-09)_CYANIDE MIDI-DISTILLATION_335.2 335.4 9012A SM 4500 CN- B SM 4500 CN-C
- GR-18-106_REV 3.1(09-14-06)_CYANIDE MACRO-DISTILLATION_9010B 4500 CN-B 4500 CN-C
- GR-05-122_REV 0.4(09-25-09)_CYANIDE KONELAB_4500-CN G 4500-CN E 9014_
- GR-01-148_REV 0.3(01-20-09)_BLOCK DIGEST ICP-MS_3020A
- GR-01-147_REV 0.4(01-20-09)_BLOCK DIGEST for ICP_200.7 3010A
- GR-01-139_REV 0.2(08-15-09)_MERCURY BLOCK DIGEST SOIL_7471A
- GR-01-138_REV 0.6(01-20-09)_MERCURY_1631E
- GR-01-137_REV 1.5(02-01-09)_BLOCK DIG SOLIDS ICP ICPMS_3050B
- GR-01-129_REV 3.8(02-01-09)_ICPMS_6020A
- GR-01-123_REV 5.6(02-01-09)_MERCURY_245.1 7470A 7471A
- GR-01-117_REV 2.7(01-20-09)_SPLP_1312
- GR-01-100_REV 5.7(02-05-09)_ICP METALS_6010C
- GR-10-104_REV 2 2(04-06-09)_CoC

ACRONYMS AND ABBREVIATIONS

%D	Percent difference
%R	Percent recovery
µg/L	Micrograms per liter
AES	Atomic emission spectroscopy
AST	Aboveground storage tank
BBL	Blasland, Bouck, & Lee
bgs	Below ground surface
CA	Corrective action
CADRE	Computer-aided data review and evaluation
CAS	Chemical Abstract Services
CCV	Continuing calibration verification
CD	Consent decree
CF	Calibration factor
CLP	Contract Laboratory Program
CRA	Conestoga-Rovers & Associates, Inc.
CRQL	Contract-required quantitation limit
DQI	Data quality indicator
EPA	United States Environmental Protection Agency
ERM	Environmental Resource Management
FORMS	Field Operations and Records Management System
FS	Feasibility study
FSP	Field sampling plan
FTC&H	Fishbeck, Thompson, Carr and Huber
GC	Gas chromatography
HAZWOPER	Hazardous Waste Operations and Emergency Response Standard
HCl	Hydrochloric acid
HNO_3	Nitric acid
ICP	Inductively coupled plasma
ID	Identification
LIMS	Laboratory information management system
MCL	Maximum contaminant level
MDEQ	Michigan Department of Environmental Quality
mg/kg	Milligrams per kilogram
mL	Milliliter
MS	Matrix spike
MSD	Matrix spike duplicate
NA	Not applicable
NC	No criteria
NFG	National Functional Guidelines
OSHA	Occupational Safety and Health Administration
OU	Operable Unit
PAH	Polycyclic aromatic hydrocarbon

PCB	Polychlorinated biphenyl
PID	Photoionization detector
PQO	Project quality objective
PRP	Potentially responsible party
PTFE	Polytetrafluoroethylene
PVOC	Petroleum-related volatile organic compounds
QA	Quality assurance
QAPP	Quality assurance project plan
QC	Quality control
QL	Quantitation limit
RAC	Remedial Action Contract
RI	Remedial investigation
RMT	RMT, Inc.
ROD	Record of Decision
RPD	Relative percent difference
RRF	Relative response factor
RSCC	Regional Sample Control Coordinator
RSD	Relative standard deviation
SAP	Sampling and analysis plan
SOP	Standard operating procedure
SOW	Statement of work
TBD	To be determined
TCE	Trichloroethene
UFP	Uniform Federal Policy for Implementing Environmental Quality Systems
UST	Underground storage tank
VOC	Volatile organic compound
WA	Work assignment
WAM	Work assignment manager
Weyerhaeuser	Weyerhaeuser Company

1.0 INTRODUCTION

SulTRAC has prepared this quality assurance project plan (QAPP) as part of the sampling and analysis plan (SAP) for the Plainwell Mill Site, Operable Unit No. 7 of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site in Plainwell, Kalamazoo County, Michigan. The QAPP was prepared under the U.S. Environmental Protection Agency (EPA) Remedial Action Contract (RAC) II for Region 5, Contract No. EP-S5-06-02, Work Assignment (WA) No. 041-RSBD-059B. The potentially responsible party (PRP) for the site is Weyerhaeuser Company (Weyerhaeuser). During the PRP remedial investigation (RI)/feasibility study (FS), SulTRAC will perform two tasks: (1) split sampling and (2) oversight of PRP field investigation. The SAP consists of the field sampling plan (FSP) (Attachment A) and the QAPP (Attachment B), which are among the site-specific plans to be prepared under the WA in accordance with Task 1 of the EPA statement of work (SOW) (EPA 2008) for the Plainwell Mill site.

This QAPP describes quality assurance (QA) and quality control (QC) protocols and objectives, methods, and procedures to be performed by SulTRAC during the RI/FS oversight activities at the Plainwell Mill Site. The purpose of the split sampling is to compare results with PRP data, and the purpose of the PRP oversight is to ensure that the PRP field investigation is conducted in accordance with the PRP's plans that are currently pending EPA approval (Conestoga-Rovers & Associates, Inc. [CRA] 2009a, b, c). The scope of the QAPP, as outlined in the SulTRAC work plan (SulTRAC 2008), has been developed in consultation with EPA, and is based on the PRP's previous RI/FS work plan (RMT 2008a) and the current PRP work plan (CRA 2009c) (the PRP recently changed environmental consultants). The goals of the RI/FS are to (1) acquire the data necessary to support selection of an approach for site remediation and then (2) use these data to support a Record of Decision (ROD).

Section 2.0 of this QAPP describes the site and its history. Section 3.0 describes procedures SulTRAC will follow in sampling and conducting oversight. References used to prepare this QAPP are listed in Section 4.0. Site figures cited in the QAPP appear after Section 4.0, followed by the QAPP worksheets. Appendix A includes standard operating procedures (SOP) of SulTRAC's subcontractor laboratory (TriMatrix Laboratories, Inc., of Grand Rapids, Michigan) for all applicable analytical methods and chain of custody.

2.0 SITE DESCRIPTION AND HISTORY

The Plainwell Paper Mill, operable unit (OU) No. 7 (the site), is an approximately 34-acre parcel located at 200 Allegan Street, Plainwell, Kalamazoo County, Michigan. The property is occupied by (1) the now vacant Plainwell Paper Mill, (2) wastewater treatment structures associated with paper manufacturing, and (3) the vacant Specialty Minerals, Inc. property. The site is currently owned by the City of Plainwell, which is discussing plans for its re-use to include utilizing the property for a new town hall and other mixed-use facilities. The site is bordered by the Kalamazoo River to the north, Mill Race and commercial properties to the east, Allegan Street (M-89) to the south with mixed residential/commercial buildings beyond this, and residential properties and the City of Plainwell Sewage Treatment Facility to the west.

2.1 SITE HISTORY

The site had been the location of papermaking operations for over 100 years beginning in 1884 at the earliest and ending in 2000 with the closing of the facility. The original footprint of the mill and the site itself had increased since inception of operations through 1995, when the Simpson Plainwell Paper Company purchased the final addition. Ownership of the property changed several times throughout the history of the site, ending in 2000 with the bankruptcy of the Simpson Plainwell Paper Company. In 2006, the site was acquired by the City of Plainwell. Weyerhaeuser, which owned the facility between 1961 and 1970, is the current PRP for the site. Weyerhaeuser was identified as a PRP for the Allied Paper site in a General Notice letter dated April 8, 2004, received by Weyerhaeuser and two other PRPs (RMT 2008a). Concurrently, Weyerhaeuser was negotiating a Consent Decree (CD) to undertake specific activities on the former Plainwell Mill and 12th Street Landfill sites. On February 22, 2005, Weyerhaeuser entered into a CD with the EPA for the Design and Implementation of Certain Response Activities at the 12th Street Landfill site (OU No. 4) and the Plainwell Mill site (OU No. 7). During Weyerhaeuser's period of ownership, lagoons previously constructed on site were used for dewatering sludge during wastewater treatment. The excavated sludge was disposed of at the 12th Street Landfill. Polychlorinated biphenyls (PCB) were released from ink involved in manufacturing and recycling carbonless copy paper from 1954 to 1971. PCBs were banned by the Toxic Substances Control Act (TSCA), enacted by Congress in 1976 and implemented in 1977.

In addition to activities conducted on site that potentially generated PCBs, coal was stored and used during operations, parts-cleaning solvents were used, and tanks containing petroleum products were

necessary for operations. As a result, in addition to PCBs, other possible contaminants at the site are volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH), and metals.
In 2009, Weyerhaeuser changed project coordinators from RMT to CRA. Subsequently, CRA submitted to EPA for review amendments to the Multi-Area QAPP and Multi-Area FSP (CRA 2009a, b), and a revised Phase II RI work plan (CRA 2009c). The site location is shown on Figure 1.

2.2 FORMER SITE INVESTIGATIONS

Previous investigations at the site have been performed in three areas of the Plainwell Mill site: (1) the former wastewater sludge dewatering lagoon and aeration basin area; (2) the north-central portion of the site, including the former coal pile storage area and the vicinity of the No. 6 fuel oil tank; and (3) the mill buildings area (RMT 2008b). Remedial actions and confirmation sampling were also performed in response to a spill near the No. 6 fuel oil tank, to elevated PCB concentrations found in a storm sewer and a former wastewater discharge pipe located on the northern side of the mill buildings, and during an Emergency Action to remove paper residuals from along the Mill Banks. One of the investigations was conducted by Blasland, Bouck & Lee (BBL), as part of the EPA-approved RI for the Allied Paper, Inc./ Portage Creek/Kalamazoo River Superfund site. For the purpose of due diligence for a prospective property transfer, other investigations were conducted by consultants to the Simpson Plainwell Paper Company, or by previous and current owners. The information was provided to the Michigan Department of Environmental Quality (MDEQ) as part of the State's baseline environmental assessment process.

Former Wastewater Sludge Dewatering Lagoon and Aeration Basin Area

Three investigations have occurred in this area, including soil sampling as part of the EPA-approved remedial investigation for the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund site, and soil and groundwater sampling as part of Phase II Environmental Site Assessments performed by Environmental Resource Management (ERM) in 1997 and by Fishbeck, Thompson, Carr & Huber (FTC&H) in 2006. The primary objective of the BBL investigation was to assess whether the Plainwell Mill may have been a potential source of PCBs to the Kalamazoo River. To achieve this objective, Geoprobe® borings were advanced in 11 of the 14 former wastewater sludge dewatering lagoons and in the former aeration basin (see Figure 2). For the investigation by ERM in 1997, the primary objectives were to determine the concentrations of metals in soil and whether contaminants present in the lagoons had adversely affected groundwater. As part of the study, shallow groundwater samples were collected from temporary wells at two locations, along with soil samples from Lagoons I, J, M, and N (see

Figure 2). In 2006, FTC&H advanced four borings and installed one shallow temporary groundwater monitoring well to verify or eliminate previously cited recognized environmental conditions in this area.

North Central Portion of the Site

Three investigations have occurred in this area of the site, including a geotechnical investigation in 1980, a Phase II Environmental Site Assessment by ERM in 1996, and post-excavation soil sampling by Taplin Environmental Services, Inc., (Taplin) and Plainwell Paper Company in 1999. The objective of the geotechnical investigation by Wilkins & Wheaton in 1980 was to visually characterize the soil located in the vicinity of the then-proposed building addition. The scope of the investigation included installing 20 soil borings. For the Phase II environmental assessment by ERM in 1996, the objective was to determine if constituents of potential concern were present in three areas in the north-central portion of the site: (1) the 200,000-gallon fuel oil aboveground storage tank (AST) area, (2) the former coal pile storage area, and (3) the area located between the former coal pile storage area and the Kalamazoo River. The scope of the ERM investigation included collection and analysis of soil and groundwater samples. Finally, following a fuel oil spill in 1999, Taplin and Plainwell Paper Company collected confirmatory samples in an area adjacent to the No. 6 fuel oil containment structure. As part of the cleanup of the spill, Taplin had removed free liquids, contaminated soil, and absorbents from the area. The scope of post-excavation soil sampling included collection of samples for analyses for petroleum-related volatile organic compounds (PVOC) and PAHs.

Mill Buildings Area

Previous investigations in this area of the site included sampling and analysis of soil in areas near former wastewater treatment operations, and of sediment contained in a storm sewer and a former wastewater discharge pipe in 1994; sampling and analysis of soil and groundwater as part of a Phase II Environmental Site Assessment performed in 1996 and 2006; and sampling of soil on the Plainwell Mill site for PCB analysis, as part of a larger investigation that focused on bank soil in the Kalamazoo River. Remediation of PCB-containing sediment in the storm sewer and former wastewater discharge pipe was also performed. The primary objectives of the BBL investigation were to determine if elevated levels of PCBs were present in soil in the area of the former primary clarifier, a possible wastewater sludge storage area, and a potential warehouse construction area; and in sediment in a storm sewer and in a former wastewater discharge pipe. The sample collected from inside the storm sewer manhole was also analyzed for dioxin congeners. For the assessment performed by ERM in 1996, the objectives were to determine if

constituents of potential concern were present in the soil near the former 300-gallon gasoline underground storage tank (UST), or in the groundwater downgradient of the former gasoline UST, kerosene UST, or diesel AST─all formerly located along the northern side of the mill buildings. The assessment by FTC&H in 2006 included groundwater sampling near the No. 6 fuel oil AST and downgradient of the AST/UST area near the mill buildings.

In a letter to Weyerhaeuser dated February 19, 2008, EPA requested additional work along the former Plainwell Mill banks (RMT 2008a), in response to discovery of elevated concentrations of PCBs and oily soil encountered along the Plainwell Mill banks during the separate Plainwell Mill Banks Emergency Response activities. In 2008, RMT dug a series of test pits along the Plainwell Mill banks. RMT also installed 12 monitoring wells and three staff gauges at the site in conducting an initial assessment of groundwater conditions. The results of RMT's 2008 sampling activities were reported to EPA in February 2009 (RMT 2009).

A preliminary list was developed of chemicals of interest potentially at concentrations hazardous to human health and the environment at the Plainwell Mill site. These chemicals of interest had been identified via previous investigations of the soil and groundwater, previous site operations, and information obtained by SulTRAC. At a minimum, semivolatile organic compounds (SVOC), metals, and PCBs are present at the site. Specific contaminants detected (in soil or groundwater) include the following:

- Antimony
- Arsenic
- Benzo(a)pyrene
- Cadmium
- Copper
- Cyanide
- Dibenxo(a,h)anthracene
- Lead
- Mercury
- PCBs
- Phenanthrene

CRA is currently Weyerhaeuser's consultant, and has submitted a revised work plan for the Phase II investigation (CRA 2009c), revised QAPP (CRA 2009a), and a revised field sampling plan (CRA 2009b). CRA's plans are currently pending EPA approval as of the preparation date of SulTRAC's SAP for EPA. All PRP and SulTRAC plans are expected to be approved prior to mobilization to the site in late

November or early December 2009 for the Phase II investigation intended to further characterize the soil, groundwater, sediment, and surface water at the site.

3.0 QUALITY ASSURANCE PROJECT PLAN PROCEDURES

This QAPP describes procedures that will be used to ensure the quality of data generated during the Plainwell Mill RI/FS oversight activities. The QAPP provides a framework for how environmental data will be collected to achieve specific project objectives, and describes procedures to be implemented in order to obtain data of known and adequate quality. This QAPP was prepared in accordance with the EPA's "Uniform Federal Policy for Quality Assurance Project Plans" (UFP) (EPA 2005a). SulTRAC also reviewed CRA's revised QAPP (CRA 2009a) submitted to EPA for additional information to be referenced in this QAPP.

RI/FS oversight activities for the Plainwell Mill site are anticipated to begin in late fall 2009. Investigations will focus on three delineated areas, as noted in CRA's Phase II work plan (CRA 2009c) for the Plainwell Mill site. Area 1 includes the lagoon area to the north and northwest part of the site and also the wooded parcel near the residential area in the southwest part of the site. Area 2 includes the northern and eastern half of the site, along the Kalamazoo River and the millrace including the old mill building (see Figure 2 in the QAPP). Area 3 includes the middle portion of the site (Specialty Minerals building, Quality Products building, parking lots).

During the field oversight activities, SulTRAC will collect groundwater and soil split samples from the PRP at sampling locations to be determined pending EPA approval of CRA's Phase II RI work plan (CRA 2009c) and FSP (CRA 2009b). The purpose of this split sampling is to verify the PRP's analytical results. From fall 2009 to March 2011, SulTRAC will collect soil and groundwater split samples at a rate of 25 percent (approximately 85 soil and nine groundwater) of CRA's samples for analyses for VOCs, semi-volatile organic compounds (SVOC), PCBs, metals, low-level mercury, cyanide, and synthetic precipitation leaching procedure (SPLP) metals and cyanide, not including quality assurance/quality control (QA/QC) samples. Field duplicates will be collected at a frequency of one for every 10 samples collected. Matrix spike and matrix spike duplicate (MS/MSD) samples will be collected at a frequency of one for every 20 samples collected. One trip blank will accompany every VOC shipment sent the laboratory.

The following QAPP worksheets describe the sampling and analysis activities and provide the required information for the Plainwell Mill site. Because SulTRAC is collecting only split samples, some worksheets (Worksheets #22, 31, and 32) will not apply.

SulTRAC intends for this QAPP to cover all split sampling activities that may occur between fall 2009 and March 2011, and for QAPP worksheets to provide as much information as possible about future activities. If any significant changes to split sampling activities occur (such as added environmental media, added analytical parameters, or increased number of split samples required), SulTRAC will identify and revise the specific QAPP worksheets affected by these changes. SulTRAC will revise the QAPP by resubmitting to EPA only the worksheets affected by the changes in sampling activity.

4.0 REFERENCES

Consetoga-Rovers & Associates, Inc (CRA). 2009a. "Multi-Area Quality Assurance Project Plan,12th Street Landfill Site (Operable Unit No. 4) and Plainwell Mill Site (Operable Unit No. 7), Allied Paper Inc. /Portage Creek/Kalamazoo River Superfund Site Allegan County, Michigan." September 23.

CRA. 2009b. "Multi-Area Field Sampling Plan,12th Street Landfill Site (Operable Unit No. 4) and Plainwell Mill Site (Operable Unit No. 7), Allied Paper Inc. /Portage Creek/Kalamazoo River Superfund Site Allegan County, Michigan." September 23.

CRA. 2009c. "Phase II Remedial Investigation Work Plan, Former Plainwell, Inc. Mill Property, Plainwell, Michigan." September 23.

Fishbeck Thompson Carr & Huber (FTC&H). 2006. "Phase II Environmental Assessment, Former Plainwell Paper Mill." October.

RMT, Inc. (RMT). 2008a. "Multi-Area Field Sampling Plan, Remedial Investigation/Feasibility Study: 12th Street Landfill, Otsego Township, Michigan. Operable Unit 4 of the Allied Paper Inc./ Portage Creek/Kalamazoo River Superfund Site." October.

RMT. 2008b. "Multi-Area Quality Assurance Project Plan, Remedial Investigation/Feasibility Study: 12th Street Landfill, Otsego Township, Michigan. Operable Unit 4 of the Allied Paper Inc. /Portage Creek/Kalamazoo River Superfund Site." November.

RMT. 2008c. "Multi-Area Quality Assurance Project Plan." 12th Street Landfill Site (Operable Unit No. 4) Kalamazoo River (Operable Unit No. 5), and Plainwell Mill Site (Operable Unit No. 7) Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site Allegan County, Michigan. Revision 2, Addendum 3. November.

RMT. 2009. Phase I Initial Groundwater and Coal Tunnel Assessment Technical Memorandum. February.

SulTRAC. 2005. Quality Assurance Project Plan, Remedial Action Contract 2 (RAC 2) Region 5. December.

SulTRAC. 2008. "Revised Work Plan, Remedial Investigation/Feasibility Study (RI/FS) Oversight Plainwell Mill Site, Operable Unit 7 of Allied Paper/Portage Creek/Kalamazoo River Site, Plainwell, Kalamazoo County, Michigan." December 30.

SulTRAC. 2009. "Revised Health and Safety Plan For Remedial Investigation/Feasibility Study (RI/FS) Oversight Activities At Plainwell Mill Site, Operable Unit No. 7 of Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site, Plainwell, Allegan County, Michigan." July 17.

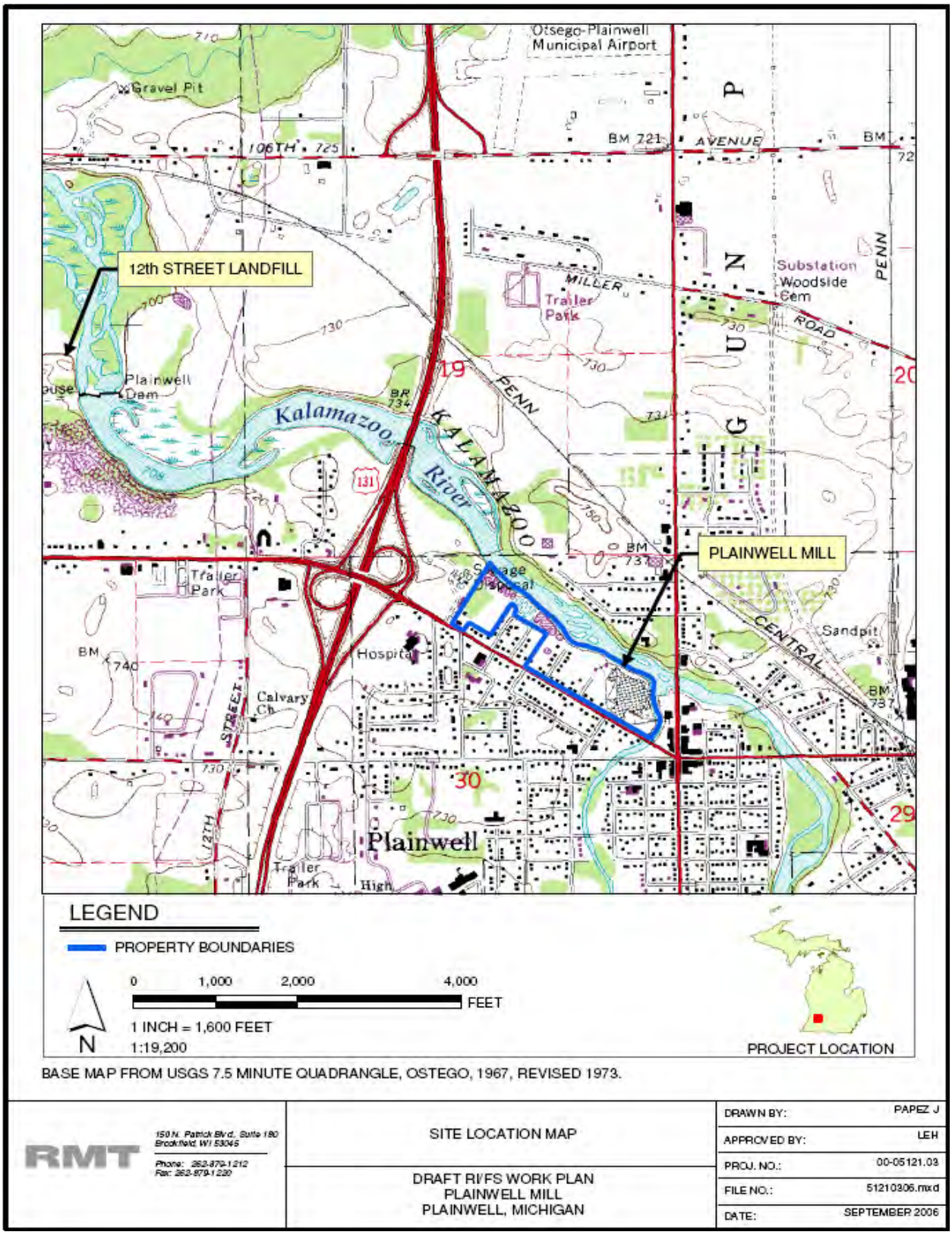
U.S. Environmental Protection Agency (EPA). 2002. "EPA Guidance for Quality Assurance Project Plans." EPA QA/G-5. December.

EPA. 2005a. "Uniform Federal Policy for Quality Assurance Project Plans Quality Systems. Part 1: UFP-QAPP Manual." EPA-505-B-04-900A. March.

EPA. 2005b. "Superfund Analytical Services/Contract Laboratory Program (CLP), Multi-Media, Multi-Concentration Organic Analysis SOM01.2." On-line address: http://www.epa.gov/superfund/programs/clp/olm4.htm. May.

EPA. 2008. "RAC II Region 5 Statement of Work for Remedial Investigation/Feasibility Study Oversight, Operable Unit #7 of the Allied Paper/Portage Creek/Kalamazoo River Site, Kalamazoo County, Michigan." November 3.

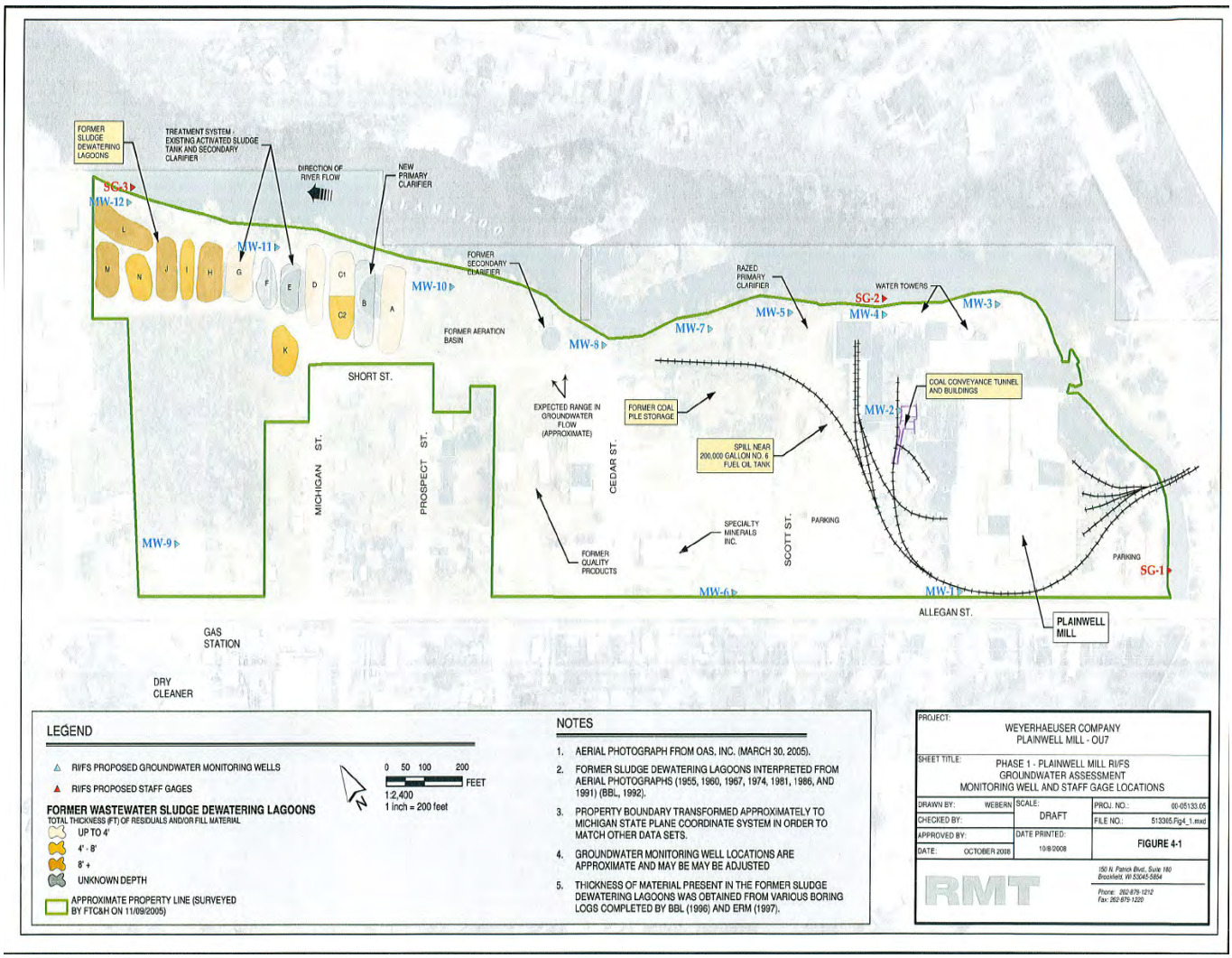
FIGURE 1
SITE LOCATION



BASE MAP FROM USGS 7.5 MINUTE QUADRANGLE, OSTEGO, 1967, REVISED 1973.

RMT 150 N. Patrick Blvd., Suite 190 Brookfield, WI 53045 Phone: 262-879-1212 Fax: 262-879-1220	SITE LOCATION MAP DRAFT RI/FS WORK PLAN PLAINWELL MILL PLAINWELL, MICHIGAN	DRAWN BY: PAPEZ J APPROVED BY: LEH PROJ. NO.: 00-05121.03 FILE NO.: 51210306.mxd DATE: SEPTEMBER 2006

FIGURE 2
SITE LAYOUT



Source for Figures 1 and 2:

Modified from RMT, Inc. 2008. "Initial Groundwater and Underground Coal Tunnel Assessment: Operable Unit 7 of the Allied Paper, Inc. / Portage Creek/Kalamazoo River Superfund Site." October.

QAPP WORKSHEET #1
TITLE AND APPROVAL PAGE

Quality Assurance Project Plan for Remedial Investigation/Feasibility Study Oversight, Plainwell Mill, Plainwell, Allegan County, Michigan

Document Title

SulTRAC

Lead Organization

Robert Kondreck, SulTRAC

Preparer's Name and Organizational Affiliation

1 South Wacker, Chicago IL 60606; (312) 201-7479; robert.kondreck@ttemi.com

Preparer's Address, Telephone Number, and E-mail Address

13 November 2009

Preparation Date (Day/Month/Year)

Jeffrey Lifka

SulTRAC Project Manager — Signature/Date

John Dirgo

SulTRAC QA Officer — Signature/Date

Approval Signatures:

Signature/Date

Sam Chummar, Work Assignment Manager

Printed Name/Title

Approval Authority
Other Approval Signatures:

Signature/Date

QAPP Reviewer

Printed Name/Title

QAPP WORKSHEET #2
QAPP IDENTIFYING INFORMATION

1. Identify guidance used to prepare QAPP:

"Uniform Federal Policy for Quality Assurance Project Plans" (UFP) (EPA 2005a) and "EPA Guidance for Quality Assurance Project Plans" (EPA 2002)

2. Identify regulatory program:

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

3. Identify approval entity: EPA Region 5

4. Indicate whether the QAPP is a generic or project-specific QAPP: Project-specific

5. List dates of scoping sessions that were held: November 20, 2008

6. List dates and titles of QAPP documents written for previous work site, if applicable: NA

7. List organizational partners (stakeholders) and connection with lead organization:

   EPA Region 5, MDEQ, SulTRAC

8. List data users: EPA Region 5, MDEQ, SulTRAC

9. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below: Because SulTRAC is collecting only split samples, some worksheets (Worksheets #22, 31, and 32) will not apply.

Identify where each required QAPP element is located in the QAPP (provide section, worksheet, table, or figure number) or other project planning documents (provide complete document title, date, section number, page numbers, and location of the information in the document). Circle QAPP elements and required information that are not applicable to the project. Provide an explanation in the QAPP.

QAPP WORKSHEET #2 (CONTINUED)
QAPP IDENTIFYING INFORMATION

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
Project Management and Objectives		
2.1 - Title and Approval Page	Title and Approval Page	1
2.2 - Document Format and Table of Contents	Table of Contents	
2.2.1 Document Control Format	QAPP Identifying Information	2
2.2.2 Document Control Numbering System		
2.2.3 Table of Contents		
2.2.4 QAPP Identifying Information		
2.3 - Distribution List and Project Personnel Sign-Off Sheet		
2.3.1 Distribution List	Distribution List	3
2.3.2 Project Personnel Sign-Off Sheet	Project Personnel Sign-Off Sheet	4
2.4 - Project Organization		
2.4.1 Project Organization Chart	Project Organization Chart	5
2.4.2 Communication Pathways	Communication Pathways	6
2.4.3 Personnel Responsibilities and Qualifications	Personnel Responsibilities and Qualifications	7
2.4.4 Special Training Requirements and Certification	Special Training Requirements and Certification	8
2.5 - Project Planning/Problem Definition		
2.5.1 Project Planning (Scoping)	Project Planning Session Documentation (including Data Needs tables)	9
	Project Scoping Session Participants Sheet	
2.5.2 Problem Definition, Site History, and Background	Problem Definition, Site History, and Background	Introduction, 10
	Site Maps (historical and present)	Figures 1 and 2 in QAPP

QAPP WORKSHEET #2 (CONTINUED)
QAPP IDENTIFYING INFORMATION

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
2.6 - Project Quality Objectives (PQO) and Measurement Performance Criteria		
2.6.1 Development of PQOs Using the Systematic Planning Process	Site-Specific PQOs	11
2.6.2 Measurement Performance Criteria	Measurement Performance Criteria Table	12
2.7 - Secondary Data Evaluation	Sources of Secondary Data and Information	13
	Secondary Data Criteria and Limitations Table	
2.8 - Project Overview and Schedule		
2.8.1 Project Overview	Summary of Project Tasks	14
	Reference Limits and Evaluation Table	15
2.8.2 Project Schedule	Project Schedule/Timeline Table	16
Measurement/Data Acquisition		
3.1 - Sampling Tasks		
3.1.1 Sampling Process Design and Rationale	Sampling Design and Rationale	17
	Sampling Location Map	Figures 1 and 2 in QAPP
	Sampling Locations and Methods/Standard Operating Procedures (SOP) Requirements Table	
3.1.2 Sampling Procedures and Requirements		
3.1.2.1 Sampling Collection Procedures	Field Quality Control Sample Summary Table	20
	Sampling SOPs	21
	Project Sampling SOP References Table	21
3.1.2.2 Sample Containers, Volume, and Preservation	Analytical Methods/SOP Requirements Table	19, 23
3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures	Analytical Methods, Containers, Preservatives, and Holding Times Table	19

QAPP WORKSHEET #2 (CONTINUED)
QAPP IDENTIFYING INFORMATION

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures	Field Equipment, Calibration, Maintenance, Testing, and Inspection Procedures Table	22
3.1.2.5 Supply Inspection and Acceptance Procedures		
3.1.2.6 Field Documentation Procedures		
3.2 - Analytical Tasks		
3.2.1 Analytical SOPs	Analytical SOPs	23
	Analytical SOP References Table	
3.2.2 Analytical Instrument Calibration Procedures	Analytical Instrument Calibration Table	24
3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures	Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	25
3.2.4 Analytical Supply Inspection and Acceptance Procedures		
3.3 - Sample Collection Documentation, Handling, Tracking, and Custody Procedures	Sample Collection Documentation Handling, Tracking, and Custody SOPs	26, FSP
3.3.1 Sample Collection Documentation	Sample Container Identification	26, 27
3.3.2 Sample Handling and Tracking System	Sample Handling Flow Diagram	
3.3.3 Sample Custody	Example Chain-of-Custody Form and Seal	
3.4 - Quality Control (QC) Samples		
3.4.1 Sampling QC Samples	QC Samples Table	28
3.4.2 Analytical QC Samples		
3.5 - Data Management Tasks		
3.5.1 Project Documentation and Records	Project Documents and Records Table	29

QAPP WORKSHEET #2 (CONTINUED)
QAPP IDENTIFYING INFORMATION

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
3.5.2 Data Package Deliverables	Analytical Services Table	30
3.5.3 Data Reporting Formats		23 (specified by analytical method) Data Management Plan
3.5.4 Data Handling and Management	Data Management SOPs	
3.5.5 Data Tracking and Control		
Assessment/Oversight		
4.1 - Assessments and Response Actions	Assessments and Response Actions	
4.1.1 Planned Assessments	Planned Project Assessments Table	31
	Audit Checklists	
4.1.2 Assessment Findings and Corrective Action (CA) Responses	Assessment Findings and CA Responses Table	32
4.2 - QA Management Reports	QA Management Reports Table	33
4.3 - Final Project Report		To be determined (TBD)
Data Review		
5.1 - Overview	Not applicable (NA)	NA
5.2 - Data Review Steps		
5.2.1 Step I: Verification	Verification (Step I) Process Table	34
5.2.2 Step II: Validation		
5.2.2.1 Step IIa Validation Activities	Validation (Steps IIa and IIb) Process Table	35
5.2.2.2 Step IIb Validation Activities	Validation (Steps IIa and IIb) Summary Table	36

QAPP WORKSHEET #2 (CONTINUED)
QAPP IDENTIFYING INFORMATION

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
5.2.3 Step III: Usability Assessment		
5.2.3.1 Data Limitations and Actions from Usability Assessment	Usability Assessment	37
5.2.3.2 Activities		
5.3 - Streamlining Data Review	NA	NA
5.3.1 Data Review Steps to be Streamlined		
5.3.2 Criteria for Streamlining Data Review		
5.3.3 Amounts and Types of Data Appropriate for Streamlining		

QAPP WORKSHEET #3
DISTRIBUTION LIST

(UFP QAPP Section 2.3.1)
List individuals who received copies of the approved QAPP, subsequent QAPP revisions, addenda, and amendments.

QAPP Recipient	Title	Organization	Telephone Number	E-mail Address
Sam Chummar	Work Assignment Manager (WAM)	EPA Region 5	(312) 886-1434	chummar.sam@epa.gov
To be determined (TBD) - EPA	QAPP Reviewer	EPA Region 5	TBD	TBD
Jeffrey Lifka	Project Manager	SulTRAC	(312) 201-7491	jeffrey.lifka@ttemi.com
Bethany Hand	Field Team Leader	SulTRAC	(312) 201-7457	bethany.hand@ttemi.com
Robert Kondreck	Project Scientist and Sample Custodian	SulTRAC	(312) 201-7479	robert.kondreck@ttemi.com
Ron Riesing	Project QC Reviewer	SulTRAC	(312) 201-7722	ronald.riesing@ttemi.com
John Dirgo	QA Officer	SulTRAC	(312) 201-7765	john.dirgo@ttemi.com
William Earle	Analytical Coordinator	SulTRAC	(312) 443-0550, ext. 12	wearle@onesullivan.com

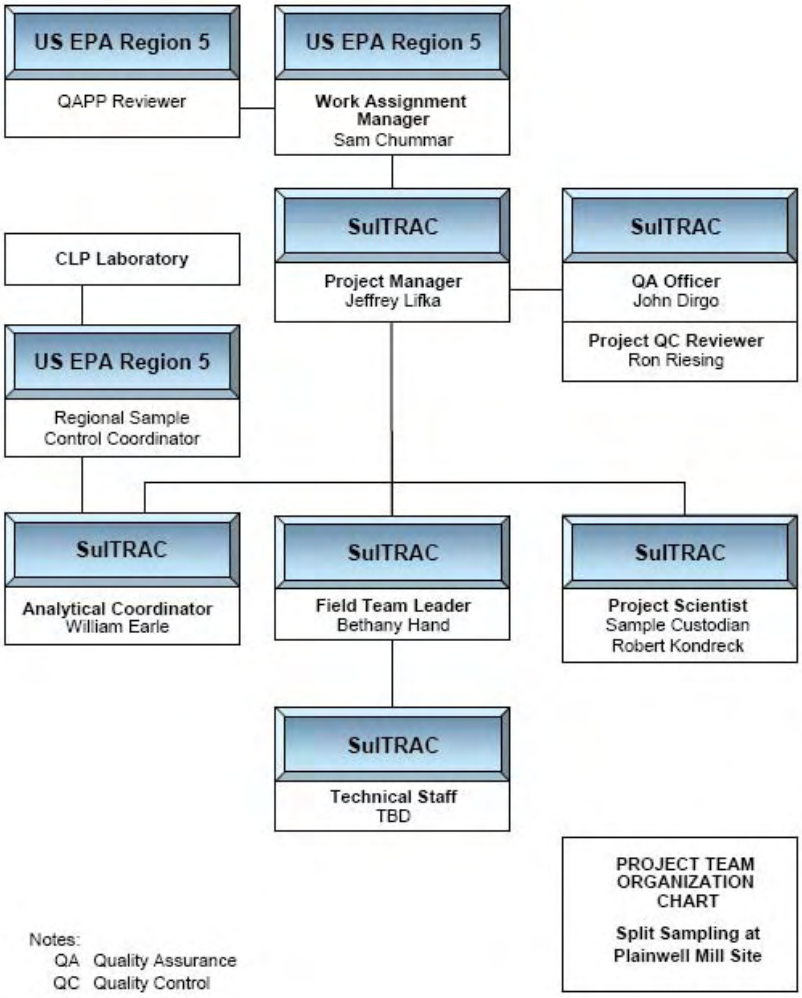
QAPP WORKSHEET #4
PROJECT PERSONNEL SIGN-OFF SHEET

(UFP QAPP Section 2.3.2)
Have copies of this form signed by key project personnel from each organization to indicate that they have read the applicable sections of the QAPP and will perform the tasks as described. Ask each organization to forward signed sheets to central project file.

Project Personnel	Organization	Title	Telephone No.	Signature	Date QAPP Read
Jeffrey Lifka	SulTRAC	Project Manager	(312) 201-7491		
William Earle	SulTRAC	Analytical Coordinator	(312) 443-0550, ext. 12		
Ron Riesing	SulTRAC	Project QA Reviewer	(312) 201-7722		
John Dirgo	SulTRAC	QA/QC Officer	(312) 201-7765		
Robert Kondreck	SulTRAC	Project Scientist and Sample Custodian	(312) 201-7479		
Bethany Hand	SulTRAC	Field Team Leader	(312) 201-7457		

QAPP WORKSHEET #5
PROJECT ORGANIZATION CHART

(UFP QAPP Section 2.4.1)
Identify reporting relationships between all organizations involved in the project, including the lead organization and all contractor and subcontractor organizations. Identify the organizations providing field sampling, on-site and off-site analysis, and data review services, including the names of project managers for each organization.



QAPP WORKSHEET #6
COMMUNICATION PATHWAYS

(UFP QAPP Section 2.4.2)

Describe the communication pathways and modes of communication that will be used during the project, after the QAPP has been approved. Describe the procedures for soliciting and/or obtaining approval between project personnel, between different contractors, and between samplers and laboratory staff. Describe the procedure that will be followed when any project activity originally documented in an approved QAPP requires real-time modification to achieve project goals or a QAPP amendment is required. Describe the procedures for stopping work and identify who is responsible.

Communication Drivers	Responsible Entity	Name	Telephone No.	Procedure (Timing, Pathways, etc.)
Point of contact with EPA WAM	Project Manager	Jeffrey Lifka	(312) 201-7491	Jeffrey Lifka will forward all materials and information about the project to Sam Chummar
Manage all project phases	Project Manager	Jeffrey Lifka	(312) 201-7491	Communicate information to project team on a timely basis. Notify EPA WAM by telephone or e-mail of any significant issues. Direct field team and facilitate communication with analytical coordinator.
Daily field progress report	Field Team Leader	Bethany Hand	(312) 201-7457	Conduct specific field investigation tasks and provide daily communication with project manager and sample custodian.
Manage field sample organization and delivery to Contract Laboratory Program (CLP) laboratories	Project Scientist and Sample Custodian	Robert Kondreck	(312) 201-7479	Ensure split samples are collected in proper containers, observing holding times, and properly packaging and preparing samples for shipment. Coordinate daily with analytical coordinator concerning sample quantities and delivery locations and dates. Communicate daily with field staff and project manager regarding any issues and developments.
Point of contact with EPA Region 5 Regional Sample Control Coordinator (RSCC)	Analytical Coordinator	William Earle	(312) 443-0550, ext. 12	Contact the RSCC before each sampling event to schedule CLP laboratory services. Notify sample custodian and project manager of any CLP issues or developments. Track all CLP data deliveries. Notify project manager and forward data to him.
Release of Analytical Data	SulTRAC Project QC Reviewer	Ron Riesing	(312) 201-7722	No analytical data can be released until validation is completed and the QC reviewer has reviewed and approved the release.
Report of laboratory data quality issues	Laboratory QA Officer	TBD	TBD	All QA/QC issues resulting from the analysis of field samples will be reported by the laboratory QA officer to the RSCC.

QAPP WORKSHEET #7
PERSONNEL RESPONSIBILITIES AND QUALIFICATIONS TABLE

(UFP QAPP Section 2.4.3)
Identify project personnel associated with each organization, contractor, and subcontractor participating in responsible roles. Include data users, decision-makers, project managers, QA officers, project contacts for organizations involved in the project, project health and safety officers, geotechnical engineers and hydrogeologists, field operation personnel, analytical services, and data reviewers. Identify project team members with an asterisk (*).

Name	Title	Organization/ Affiliation	Responsibilities	Education and Experience Qualifications
Jeffrey Lifka*	Project Manager	SulTRAC	Manages project; coordinates with lead agency; manages field staff; coordinates review of CLP data deliverables with analytical coordinator; prepares and submits reports to lead agency	B.S. Biology, M.S. Environmental Engineering, 15 years of experience
Bethany Hand*	Field Team Leader	SulTRAC	Supervises field sampling and coordinates all field activities; daily reporting to project manager while conducting field activities	B.S. Microbiology, M.S. Public Health, 1 year of experience
Robert Kondreck*	Project Scientist Sample Custodian	SulTRAC	Prepares QAPP; implements field plan; verifies sample processing, packaging, and shipping	B.S. Geology, 4 years of experience
Ron Riesing	Project QC Reviewer	SulTRAC	QA/QC oversight	M.S. Engineering, 38 years of experience
John Dirgo	QA Officer	SulTRAC	QA/QC oversight	B.S. Biology; M.S. and Sc.D. Environmental Health Sciences; 30 years of experience
William Earle*	Analytical Coordinator	SulTRAC	Coordinates sample scheduling; verifies sample chain of custody; reviews computer-aided data review and evaluation (CADRE) results and data from subcontracted laboratories; notifies sample custodian and project manager of any issues or developments	B.S. Civil Engineering, Professional Engineer, 17 years of experience
TBD*	Technical Staff	SulTRAC	Implements field plan	TBD

QAPP WORKSHEET #8
SPECIAL PERSONNEL TRAINING REQUIREMENTS TABLE

(UFP QAPP Section 2.4.4)
Provide the following information for those projects requiring personnel with specialized training. Attach training records and/or certificates to the QAPP or note their location.

Project Function	Specialized Training – Title or Description of Course*	Training Provider	Training Date	Personnel/Groups Receiving Training	Personnel Titles/ Organizational Affiliation	Location of Training Records/Certificates
Field Staff	40-hour and 8-hour refresher - OSHA HAZWOPER training	Various	Various	SulTRAC	SulTRAC	Corporate human resources office

Notes:

*	Training certificates can be obtained by contacting the project manager
HAZWOPER	Hazardous Waste Operations and Emergency Response Standard
OSHA	Occupational Safety and Health Administration

QAPP WORKSHEET #9
PROJECT SCOPING SESSION PARTICIPANTS SHEET

(UFP QAPP Section 2.5.1)
Complete this worksheet for each project scoping session held. Identify project team members who are responsible for planning the project.

Project Name	RI/FS Oversight for Plainwell Mill Site	Site Name	Plainwell Mill Site, Operable Unit No. 7 Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site
Projected Date(s) of Sampling	Spring 2009 to March 2011	Site Location	Plainwell, Allegan County, Michigan
Project Manager	Jeffrey Lifka		
Date of Session	November 20, 2008		
Scoping Session Purpose:	Define scope of project		

Name	Title	Affiliation	Phone #	E-Mail Address	Project Role
Norvelle Merrill-Crawford	EPA Contracting Officer	EPA	(312) 886-6271	merrill-crawford.norvelle@epa.gov	Contracting Officer
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QAPP WORKSHEET #10
PROBLEM DEFINITION

(UFP QAPP Section 2.5.2)
Clearly define the problem and the environmental questions that should be answered for the current investigation and develop the project decision "If..., then..." statements in the QAPP, linking data results with possible actions. The prompts below are meant to help the project team define the problem. They are not comprehensive.

The problem to be addressed by the project: As stated in CRA's QAPP worksheet #10 (CRA2009a): As approved by U.S. EPA on August 6, 2008, the Remedial Investigation is being implemented in a phased approach. The Phase II RI Work Plan is in accordance with Statement of Work (SOW) for the Remedial Investigation and Feasibility Study and the terms of the Consent Decree for the Design and Implementation of Certain Response Actions at Operable Unit #4 and the Plainwell, Inc Mill Property of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site (Consent Decree), which became effective February 22, 2005. From the early 1950s to 1970s carbonless papers were recycled at the mill, a process that released a waste stream containing PCBs to Kalamazoo River. In addition until the early 1950s, wastewater from paper making operations were discharged directly to the Kalamazoo River. By the mid-1950s, wastewater treatment facilities were in place at the Site and in late 1960s the treatment facilities improved. In early 1980s, the treatment facilities were improved by construction of a new wastewater treatment facility, consisting of a new primary clarifier, a mechanical dewatering system, a new secondary clarifier, and an activated sludge treatment system. The Phase II RI Work Plan includes field sampling and analysis activities, consisting of a soil and supplemental groundwater investigation, which are required to complete the RI pursuant to the SOW, and constitutes the final phase of the RI (CRA 2009a). As per SulTRAC's EPA SOW (EPA 2008) for performing oversight of the PRP, SulTRAC will address any inconsistencies between the approved project plans and the actual activities being conducted in the field by CRA. In addition, SulTRAC will address the quality of PRP laboratory data by collecting split samples for comparison.
The environmental questions being asked: Has the PRP conducted RI/FS investigations in accordance with its approved project plans? Are the PRP's laboratory analytical results accurate?
Observations from any site reconnaissance reports: Possible presence of floating product. Elevated concentrations of PCBs and an oily substance (RMT 2008a).
A synopsis of secondary data or information from site reports: See Worksheet #13
The possible classes of contaminants and the affected matrices: Soil, sediment, surface, and groundwater samples may be analyzed for PCBs, VOCs, SVOCs, and metals.
Project decision conditions ("If…, then…" statements): If the split sampling analytical results do not compare to the PRP's analytical results based on modeling, then further QA/QC evaluation will occur. If the PRP is conducting activities contrary to the EPA-approved PRP work plan, the project manager and EPA will be notified.

QAPP WORKSHEET #11
PROJECT QUALITY OBJECTIVES/SYSTEMATIC PLANNING PROCESS STATEMENTS

(UFP QAPP Section 2.6.1)
Use this worksheet to develop PQOs in terms of type, quantity, and quality of data determined using a systematic planning process. Provide a detailed discussion of PQOs in the QAPP. List the PQOs in the form of qualitative and quantitative statements. These statements should answer questions such as those listed below. These questions are examples only; however, they are neither inclusive nor appropriate for all projects.

Who will use the data: EPA Region 5, MDEQ, and SulTRAC will use the data.
What will the data be used for? The PRP soil data will be used to determine immediate actions required and how the next phase of the investigation should be integrated with other RI activities. The PRP soil data will also be used to determine the chemical makeup of the oily substance and determine whether potential NAPLs are entering the river. Based on soil data, the source of the contamination may be determined (RMT 2008c). The PRP groundwater data will be used to identify any data gaps that must be addressed during a Phase II investigation of soil and groundwater (RMT 2008c). The PRP data obtained during the groundwater sampling will be used to (1) determine the direction of groundwater flow on the Plainwell Mill site and relationship with the Kalamazoo River and Mill Race, (2) evaluate the relationship between the elevation of onsite fill and residual materials and the groundwater table, (3) evaluate potential for groundwater impacts associated with historic site operations, (4) compare the data to MDEQ Part 201 criteria, and (5) refine the list of contaminants of potential concern for future sample analysis (RMT 2008a). CRA is implementing the Phase II investigation in November or December 2009. According to CRA's QAPP Worksheet #10 (CRA 2009a), the Phase II RI Work Plan includes field sampling and analysis activities—consisting of a soil and supplemental groundwater investigation required to complete the RI pursuant to the SOW—and constitutes the final phase of the RI (CRA 2009a).

QAPP WORKSHEET #11 (CONTINUED)
PROJECT QUALITY OBJECTIVES/SYSTEMATIC PLANNING PROCESS STATEMENTS

What type of data are needed (target analytes, analytical groups, field screening, on-site analytical or off-site laboratory techniques, sampling techniques)? The PRP will conduct a test pit investigation to collect soil samples for PCB, PAHs, VOCs, and metal laboratory analyses. In addition, the PRP will use a photoionization detector (PID) to field screen the samples. The PRP will collect groundwater samples for laboratory analyses for PCBs, PAHs, VOCs, and metals (RMT 2008a). Sediment and surface water may be sampled. Sediment and surface water investigations may be included as part of additional sampling for the RI/FS investigation. SulTRAC will collect split samples from 25 percent of the PRP's investigative samples. SulTRAC's split samples will be submitted to a CLP and subcontractor laboratory for analysis. The PRP is responsible for collecting soil, sediment, and water samples, and sample collection methods are described in the PRP's planning documents. SulTRAC will collect samples for VOCs, SVOCs, PCBs, metals, low-level mercury, cyanide, and SPLP metals and cyanide analyses. SulTRAC will sample for SVOCs instead of the PAH per CLP analytical methods and the request of the EPA WAM. Split sampling techniques will depend on the PRP's sampling methods. SulTRAC will work with the PRP sampling personnel to ensure that primary and split samples are equivalent.
How "good" do the data need to be in order to support the environmental decision? The split sample data must be sufficiently accurate and precise to assess the validity and accuracy of the soil, sediment, and water analytical data obtained by the PRP.
How much data are needed (number of samples for each analytical group, matrix, and concentration)? SulTRAC will collect approximately 81 soil/sediment and 11 water split samples from various locations. Investigative sample locations will be determined by the PRP, and SulTRAC will select locations for split sample collection. In addition, SulTRAC will collect about 24 QC samples, including trip blanks, field duplicate samples, and MS/MSD samples for laboratory analysis.
Where, when, and how should the data be collected/generated? Beginning in fall 2009, SulTRAC will collect split samples from 81 soil locations and 11 groundwater and surface water locations for laboratory analyses for PCBs, VOCs, SVOCs, metals, low-level mercury, cyanide, and SPLP metals and cyanide. Samples will be collected from locations to be determined in the field and based on CRA's field sampling plan (CRA 2009b).
Who will collect and generate the data? SulTRAC will collect the samples discussed herein. Soil and water samples will be analyzed by a laboratory from the EPA Contract Laboratory Program (CLP) and a subcontractor laboratory, TriMatrix Laboratories, Inc. (TriMatrix).
How will the data be reported? Data will be reported by the CLP laboratory and TriMatrix using standard data reporting techniques. Data will be reported in electronic and hard-copy form.
How will the data be archived? Electronic and hard copies of CLP and TriMatrix analytical data will be archived by the individual laboratory. Electronic and hard copies of laboratory data will also be archived by the SulTRAC analytical coordinator. Field data (notebooks, sampling sheets, etc.) will be maintained at SulTRAC's Chicago office. SulTRAC will also provide 10-year data storage.

QAPP WORKSHEET #12
MEASUREMENT PERFORMANCE CRITERIA TABLE

(UFP QAPP Section 2.6.2)

Complete this worksheet for each matrix, analytical group, and concentration level. Identify the data quality indicators (DQIs), measurement performance criteria (MPC) (percent recovery (% R), and relative percent difference (% RPD), and QC sample and/or activity used to assess the measurement performance for both the sampling and analytical measurement systems. Use additional worksheets if necessary. If MPC for a specific DQI vary within an analytical parameter, i.e., MPC are analyte-specific, then provide analyte-specific MPC on an additional worksheet.

Matrix	Soil/Solids[1]
Analytical Group[2]	CLP VOCs
Concentration Level	Low concentration

Sampling Procedure[3]	Analytical Method SOP[4]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-1, S-2, S-3	A-1	Precision	RPD ≤ 50%	Field duplicate	S & A
S-1, S-2, S-3	A-1	Accuracy/ Bias-Contamination	VOC < QL	Trip blank	S & A
S-1, S-2, S-3	A-1	Accuracy	Vinyl chloride-d_3: 68-122 %R Chloroethane-d_5: 61-130 %R 1,1-Dichloroethene-d_2: 45-132 %R 2-Butanone-d_5: 20-182 %R Chloroform-d: 72-123 %R 1,2-Dichloroethane-d_4: 79-122 %R Benzene-d_6: 80-121 %R 1,2-Dichloropropane-d_6: 74-124 %R Toluene-d_8: 78-121 %R 1,1,2,2-Tetrachloroethane-d_2: 56-161 %R Trans-1,3-Dichloropropene-d_4: 72-130 %R 2-Hexanone-d_5: 17-184 %R 1,4-Dioxane-d_8: 50-150 %R 1,2-Dichlorobnzene-d_4: 70-131 %R	Deuterated monitoring compounds	A
S-1, S-2, S-3	A-1	Accuracy/Bias	1,1-Dichloroethene: 59-172 %R TCE: 62-137 %R Benzene: 66-142 %R Toluene: 59-139 %R Chlorobenzene: 60-133 %R	MS/MSD	S & A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Soil/Solids[1]
Analytical Group[2]	CLP VOCs
Concentration Level	Low concentration

Sampling Procedure[3]	Analytical Method SOP[4]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-1, S-2, S-3	A-1	Precision	1,1-Dichloroethene: 22% RPD TCE: 24% RPD Benzene: 21% RPD Toluene: 21% RPD Chlorobenzene: 21% RPD	MS/MSD	S & A
S-1, S-2, S-3	A-1	Accuracy/ Bias-Contamination	VOC < QL	Method blank	A
S-1, S-2, S-3	A-1	Completeness	≥ 90%	Data completeness defined as data not qualified as rejected after validation	S&A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Soil[1]
Analytical Group[2]	CLP SVOCs
Concentration Level	Low concentration

Sampling Procedure[3]	Analytical Method SOP[4]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-1, S-2, S-3	A-1	Precision	RPD ≤ 50%	Field duplicate	S & A
S-1, S-2, S-3	A-1	Accuracy/ Bias-Contamination	SVOC < QL	Rinsate blank	S & A
S-1, S-2, S-3	A-1	Accuracy/Bias	Phenol: 26-90 %R 2-Chlorophenol: 25-102 %R N-Nitroso-di-n-propylamine: 41-126 %R 4-Chloro-3-methylphenol: 26-103 %R Acenaphthene: 31-137 %R 4-Nitrophenol: 11-114 %R 2,4-Dinitrotoluene: 28-89 %R Pentachlorophenol: 17-109 %R Pyrene: 35-142 %R	MS/MSD	S & A
S-1, S-2, S-3	A-1	Precision	Phenol: 35% RPD 2-Chlorophenol: 50% RPD N-Nitroso-di-n-propylamine: 38% RPD 4-Chloro-3-methylphenol: 33% RPD Acenaphthene: 19% RPD 4-Nitrophenol: 50% RPD 2,4-Dinitrotoluene: 47% RPD Pentachlorophenol: 47% RPD Pyrene: 36% RPD	MS/MSD	S & A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Soil[1]
Analytical Group[2]	CLP SVOCs
Concentration Level	Low concentration

Sampling Procedure[3]	Analytical Method SOP[4]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-1, S-2, S-3	A-1	Accuracy	Phenol-d_5: 17-103 %R Bis(2-Chloroethyl)ether-d_8: 12-98 %R 2-Chlorophenol-d_4: 13-101 %R 4-Methylphenol-d_8: 8-100 %R Nitrobenzene-d_5: 16-103 %R 2-Nitrophenol-d_4: 16-104 %R 2,4-Dichlorophenol-d_3: 23-104 %R 4-Chloroaniline-d_4: 1-145 %R Dimethylphthalate-d_6: 43-111 %R Acenaphthylene-d_8: 20-97 %R 4-Nitrophenol-d_4: 16-166 %R Fluorene-d_{10}: 40-108 %R 4,6-Dinitro-2-methylphenol-d_2: 1-121 %R Anthracene-d_{10}: 22-98 %R Pyrene-d_{10}: 51-120 %R Benzo(a)pyrene-d_{12}: 43-111 %R	Deuterated monitoring compounds	A
S-1, S-2, S-3	A-1	Accuracy/Bias-Contamination	SVOC < QL	Method blank	A
S-1, S-2, S-3	A-1	Completeness	≥ 90%	Data completeness defined as data not qualified as rejected after validation	S&A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Soil/Solids[1]
Analytical Group[2]	CLP PCBs
Concentration Level	NA[5]

Sampling Procedure[3]	Analytical Method SOP[4]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-1, S-2, S-3	A-1	Precision	RPD ≤ 50%	Field duplicate	S & A
S-1, S-2, S-3	A-1	Accuracy/Bias	Aroclor-1016: 29-135 %R Aroclor-1260: 29-135 %R	MS/MSD	S & A
S-1, S-2, S-3	A-1	Precision	Aroclor-1016: 15% RPD Aroclor-1260: 20% RPD	MS/MSD	S & A
S-1, S-2, S-3	A-1	Accuracy	Decachlorobiphenyl: 30-150 %R, Tetrachloro-m-xylene: 30-150 %R	Surrogate spike	A
S-1, S-2, S-3	A-1	Accuracy/ Bias-Contamination	PCB < QL	Method blank	A
S-1, S-2, S-3	A-1	Completeness	≥ 90%	Data completeness defined as data not qualified as rejected after validation	S & A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Soil/Solids[1]
Analytical Group[2]	Metals and Cyanide
Concentration Level	NA[5]

Sampling Procedure[3]	Analytical Method SOP[4]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-1, S-2, S-3	A-2	Precision	RPD ≤ 50%	Field duplicate	S & A
S-1, S-2, S-3	A-2	Accuracy/Bias	Metals and cyanide: 75-125 %R	MS	S & A
S-1, S-2, S-3	A-2	Precision	Metals and cyanide: < 20% RPD	Laboratory duplicate	S & A
S-1, S-2, S-3	A-2	Accuracy	Metals and cyanide: 80-120 %R	Laboratory control sample	A
S-1, S-2, S-3	A-2	Sensitivity/Contamination	Metals and cyanide <QL	Method blank	A
S-1, S-2, S-3	A-2	Completeness	≥ 90%	Data completeness defined as data not qualified as rejected after validation	S&A

%R Percent recovery
CLP Contract laboratory program
DQI Data quality indicator
MS/MSD Matrix spike/Matrix spike duplicate
PCB Polychlorinated biphenyl
QL Quantitation limit
RPD Relative percent difference
SOP Standard operating procedures
TCE Trichloroethene
VOC Volatile organic compound

1 Soils/solids include native and fill material and sediment.
2 If information varies within an analytical group, separate by individual analyte.
3 Reference number from QAPP Worksheet #21
4 Reference number from QAPP Worksheet #23
5 Not applicable, only one concentration level is listed for the analytical method selected

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Water
Analytical Group[1]	CLP VOCs
Concentration Level	Low concentration

Sampling Procedure[2]	Analytical Method SOP[3]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-4, S-5	A-1	Precision	RPD ≤ 50%	Field duplicate	S & A
S-4, S-5	A-1	Accuracy/ Bias-Contamination	VOC < QL	Trip blank	S & A
S-4, S-5	A-1	Accuracy/Bias	1,1-Dichloroethene: 61-145 %R TCE: 71-120 %R Benzene: 76-127 %R Toluene: 76-125 %R Chlorobenzene: 75-130 %R	MS/MSD	S & A
S-4, S-5	A-1	Precision	1,1-Dichloroethene: 14% RPD TCE: 14% RPD Benzene: 11% RPD Toluene: 13% RPD Chlorobenzene: 13% RPD	MS/MSD	S & A
S-4, S-5	A-1	Accuracy	Vinyl chloride-d_3: 65-131 %R Chloroethane-d_5: 71-131 %R 1,1-Dichloroethene-d_2: 55-104 %R 2-Butanone-d_5: 49-155 %R Chloroform-d: 78-121 %R 1,2-Dichloroethane-d_4: 78-129 %R Benzene-d_6: 77-121 %R 1,2-Dichloropropane-d_6 : 79-124 %R Toluene-d_8 : 77-121 %R 1,1,2,2-Tetrachloroethane-d_2: 73-125 %R Trans-1,3-Dichloropropene-d_4: 73-121 %R 2-Hexanone-d_5: 28-135 %R 1,4-Dioxane-d_8: 50-150 %R 1,2-Dichlorobnzene-d_4: 80-131 %R	Deuterated monitoring compounds	A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Water
Analytical Group[1]	CLP VOCs
Concentration Level	Low concentration

Sampling Procedure[2]	Analytical Method SOP[3]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-4, S-5	A-1	Accuracy/ Bias-Contamination	VOC < QL	Method blank	A
S-4, S-5	A-1	Completeness	≥ 90%	Data completeness defined as data not qualified as rejected after validation	S & A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Water
Analytical Group[1]	CLP SVOCs
Concentration Level	Low concentration

Sampling Procedure[2]	Analytical Method SOP[3]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-4, S-5	A-1	Precision	RPD ≤ 50%	Field Duplicate	S & A
S-4, S-5	A-1	Accuracy/Bias-Contamination	SVOC < QL	Rinsate blank	S & A
S-4, S-5	A-1	Accuracy/Bias	Phenol: 12-110 %R 2-Chlorophenol: 27-123 %R N-Nitroso-di-n-propylamine: 41-116 %R 4-Chloro-3-methylphenol: 23-97 %R Acenaphthene: 46-118 %R 4-Nitrophenol: 10-80 %R 2,4-Dinitrotoluene: 24-96 %R Pentachlorophenol: 9-103 %R Pyrene: 26-127 %R	MS/MSD	S & A
S-4, S-5	A-1	Precision	Phenol: 42% RPD 2-Chlorophenol: 40% RPD N-Nitroso-di-n-propylamine: 38% RPD 4-Chloro-3-methylphenol: 42% RPD Acenaphthene: 31% RPD 4-Nitrophenol: 50% RPD 2,4-Dinitrotoluene: 38% RPD Pentachlorophenol: 50% RPD Pyrene: 31% RPD	MS/MSD	S & A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Water
Analytical Group[1]	CLP SVOCs
Concentration Level	Low concentration

Sampling Procedure[2]	Analytical Method SOP[3]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-4, S-5	A-1	Accuracy	Phenol-d_5: 39-106 %R Bis(2-chloroethyl)ether-d_8: 40-105 %R 2-Chlorophenol-d_4: 41-106 %R 4-Methylphenol-d_8: 25-111 %R Nitrobenzene-d_5: 43-108 %R 2-Nitrophenol-d_4: 40-108 %R 2,4-Dichlorophenol-d_3: 37-105 %R 4-Chloroaniline-d_4: 1-145 %R Dimethylphthalate-d_6: 47-114 %R Acenaphthylene-d_8: 41-107 %R 4-Nitrophenol-d_4: 33-116 %R Fluorene-d_{10}: 42-111 %R 4,6-Dinitro-2-methylphenol-d_2: 22-104 %R Anthracene-d_{10}: 44-110 %R Pyrene-d_{10}: 52-119 %R Benzo(a)pyrene-d_{12}: 32-121 %R Fluoranthene-d_{10}: 50-150 %R 2-Methylnaphthalene-d_{10}: 50-150 %R	Deuterated monitoring compounds	A
S-4, S-5	A-1	Accuracy/ Bias-Contamination	SVOC < QL	Method blank	A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Water
Analytical Group[1]	CLP SVOCs
Concentration Level	Low concentration

Sampling Procedure[2]	Analytical Method SOP[3]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-4, S-5	A-1	Completeness	≥ 90%	Data completeness defined as data not qualified as rejected after validation	S & A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Water
Analytical Group[1]	CLP PCBs
Concentration Level	NA[4]

Sampling Procedure[2]	Analytical Method SOP[3]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-4, S-5	A-1	Precision	RPD ≤ 50%	Field duplicate	S & A
S-4, S-5	A-1	Accuracy/Bias	Aroclor-1016: 29-135 %R Aroclor-1260: 29-135 %R	MS/MSD	S & A
S-4, S-5	A-1	Precision	Aroclor-1016: 15% RPD Aroclor-1260: 20% RPD	MS/MSD	S & A
S-4, S-5	A-1	Accuracy	Decachlorobiphenyl: 30-150 %R Tetrachloro-m-xylene: 30-150 %R	Surrogate spike	A
S-4, S-5	A-1	Accuracy/ Bias-Contamination	PCB < QL	Method blank	A
S-4, S-5	A-1	Completeness	≥ 90%	Data completeness defined as data not qualified as rejected after validation	S & A

QAPP WORKSHEET #12 (CONTINUED)
MEASUREMENT PERFORMANCE CRITERIA TABLE

Matrix	Water[5]
Analytical Group[1]	Metals and cyanide
Concentration Level	NA[4]

Sampling Procedure[2]	Analytical Method SOP[3]	DQIs	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
S-4, S-5	A-2	Precision	RPD ≤ 50%	Field duplicate	S & A
S-4, S-5	A-2	Accuracy	Metals and cyanide: 75-125 %R	MS	A
S-4, S-5	A-2	Precision	Metals and cyanide: < 20% RPD	Laboratory duplicate	A
S-4, S-5	A-2	Accuracy	Metals and cyanide: 80-120 %R	Laboratory control sample	A
S-4, S-5	A-2	Sensitivity/Contamination	Metals and cyanide < QL	Method blank	A
S-4, S-5	A-2	Completeness	≥ 90%	Data completeness defined as data not qualified as rejected after data validation	S&A

Notes:

%R	Percent recovery
CLP	Contract laboratory program
DQI	Data quality indicator
MS/MSD	Matrix spike/Matrix spike duplicate
PCB	Polychlorinated biphenyl
QL	Quantitation limit
RPD	Relative percent difference
SOP	Standard operating procedures
TCE	Trichloroethene
VOC	Volatile organic compound

[1] If information varies within an analytical group, separate by individual analyte.
[2] Reference number from QAPP Worksheet #21
[3] Reference number from QAPP Worksheet #23
[4] Not applicable, only one concentration level is listed for the analytical method selected
[5] Includes Synthetic Precipitation Leaching Procedure (SPLP) extract

QAPP WORKSHEET #13
SECONDARY DATA CRITERIA AND LIMITATIONS TABLE

(UFP QAPP Section 2.7)
Identify all secondary data and information that will be used for the project and their originating sources. Specify how the secondary data will be used and the limitations on their use.

Secondary Data[1]	Data Source (Originating Organization, Report Title, and Date)	Data Source (Originating Org, Data Types, data Generation/Collection Dates)	How data will be used	Limitation on Data Use
Soil and groundwater sampling data	FTC&H. "Phase II Environmental Assessment, Former Plainwell Paper Mill." October 2006 (FTC&H 2006)	FTC&H; soil and groundwater samples; collected in 2006	Further evaluate the recognized environmental conditions	None
Groundwater sampling data	RMT. "Plainwell Mill RI/FS Phase I Work Plan Groundwater Investigation/Coal Tunnel Assessment Operable Unit No.7 of the Allied Paper, Inc./Portage Creek/Kalamazoo River Superfund Site." October 2008 (RMT 2008b)	RMT; groundwater samples; collected in 2006 and 1997	Historical groundwater monitoring data (1997 and 2006)	None
	RMT. GW/Coal Tunnel data. (Feb 2009)	RMT; groundwater samples; collected in December 2008	To plan Phase II investigation	None

Notes:

FTC&H Fishbeck, Thompson, Carr, and Huber

[1] As discussed in Section 2.0, several previous investigations have been conducted at the site; the two most recent investigations are listed in Worksheet #13.

QAPP WORKSHEET #14
SUMMARY OF PROJECT TASKS

(UFP QAPP Section 2.8.1)
Provide a brief overview of the listed project activities.

Sampling Tasks: 1 - Collect 81 soil and 11 split water samples from the PRP at designated locations 2 - Take digital photographs to document activities. 3 - Log activities and tasks in a field notebook. 4 - Prepare sample documentation such as chain-of-custody forms, sample labels, custody seals, etc.
Analysis Tasks: The CLP laboratory will analyze samples for VOCs, SVOCs, and PCBs; TriMatrix will analyze samples for metals, cyanide, low-level mercury and SPLP metals and cyanide.
QC Tasks: The following QC samples will be collected and analyzed during the sampling event: field duplicates, MS/MSD samples, and and trip blanks.
Secondary Data: See Worksheet #13
Data Management Tasks: Analytical data will be archived in an electronic database after validation.
Documentation and Records: All samples collected will be documented in a logbook using a ballpoint pen. The time of collection, identification number, sampling location, field observations, sampler's name, and analyses will be recorded in the logbook for each sample. Each page of the logbook will be dated, numbered, and signed by SulTRAC personnel. Field data records will be maintained at SulTRAC's Chicago office. SulTRAC will follow custody procedures outlined in SulTRAC's program-level QAPP for the RAC 2 contract (SulTRAC 2005). Further specifications are described in the Field Sampling Plan (FSP), Attachment A of the SAP.
Assessment/Audit Tasks: No assessments or audits are planned as part of this project.
Data Review Tasks: EPA will perform limited computer-aided data review and evaluation (CADRE) for all CLP data, and will prepare a case narrative detailing any issues or inconsistencies discovered. The SulTRAC analytical coordinator or project manager will review the case narrative and will detail any analytical issues that may affect data quality.

QAPP WORKSHEET #15
REFERENCE LIMITS AND EVALUATION TABLE

(UFP QAPP Section 2.8.1)
Complete this worksheet for each matrix.
Identify the target analytes/contaminants of concern and project-required action limits. Next, determine the QLs that must be met to achieve the PQOs. Finally, list the published and achievable detection and QLs for each analyte.

Reference Limits Table – Soil

Analytical Group	Analyte	CAS Number	Project Action Limit - Soil (mg/kg)[1]	CRQL - Soil (mg/kg)[2]
VOC/CLP	Dichlorodifluoromethane	75-71-8	5.0E-02	5.0E-03
VOC/CLP	Chloromethane	74-87-3	1.7E+00	5.0E-03
VOC/CLP	Vinyl chloride	75-01-4	5.0E-02	5.0E-03
VOC/CLP	Trichlorofluoromethane	75-69-4	5.0E-02	5.0E-03
VOC/CLP	Bromomethane	74-83-9	5.0E-02	5.0E-03
VOC/CLP	Chloroethane	75-00-3	5.0E-02	5.0E-03
VOC/CLP	1,1-Dichloroethene	75-35-4	4.3E+04	5.0E-03
VOC/CLP	1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	2.0E+00	5.0E-03
VOC/CLP	Acetone	67-64-1	5.0E-02	1.0E-02
VOC/CLP	Carbon disulfide	75-15-0	7.8E+04	5.0E-03
VOC/CLP	Methyl acetate	79-20-9	2.0E-01	5.0E-03
VOC/CLP	Methylene chloride	75-09-2	5.0E-02	5.0E-03
VOC/CLP	trans-1,2-Dichloroethene	156-50-5	5.0E-02	5.0E-03
VOC/CLP	Methyl tert-butyl ether	1634-04-4	5.0E-02	5.0E-03
VOC/CLP	1,1-Dichloroethane	75-34-3	5.0E-02	5.0E-03
VOC/CLP	cis-1,2-Dichloroethene	156-59-2	2.0E+00	5.0E-03
VOC/CLP	2-Butanone	78-93-3	NC	1.0E-02
VOC/CLP	Bromochloromethane	74-97-5	5.0E-02	5.0E-03
VOC/CLP	Chloroform	67-66-3	5.0E-02	5.0E-03
VOC/CLP	1,1,1-Trichloroethane	71-55-6	7.2E+03	5.0E-03
VOC/CLP	Cyclohexane	110-82-7	5.0E-02	5.0E-03
VOC/CLP	Carbon tetrachloride	56-23-5	5.0E-02	5.0E-03
VOC/CLP	Benzene	71-43-2	5.0E-02	5.0E-03

QAPP WORKSHEET #15 CONTINUED
REFERENCE LIMITS AND EVALUATION TABLE

Analytical Group	Analyte	CAS Number	Project Action Limit - Soil (mg/kg)[1]	CRQL - Soil (mg/kg)[2]
VOC/CLP	1,2-Dichloroethane	107-06-2	5.0E-02	5.0E-03
VOC/CLP	1,4-Dioxane	123-91-1	4.4E+01	1.0E-01
VOC/CLP	Trichloroethene	79-01-6	5.0E-02	5.0E-03
VOC/CLP	Methylcyclohexane	108-87-2	3.4E+03	5.0E-03
VOC/CLP	1,2-Dichloropropane	78-87-5	5.0E-02	5.0E-03
VOC/CLP	Bromodichloromethane	75-27-4	5.0E-02	5.0E-03
VOC/CLP	cis-1,3-Dichloropropene	542-75-6	5.0E-02	5.0E-03
VOC/CLP	4-Methyl-2-pentanone	108-10-1	2.0E+00	1.0E-02
VOC/CLP	Toluene	108-88-3	5.0E-02	5.0E-03
VOC/CLP	trans-1,3-Dichloropropene	10061-02-6	5.0E-02	5.0E-03
VOC/CLP	1,1,2-Trichloroethane	79-00-5	5.0E-02	5.0E-03
VOC/CLP	Tetrachloroethene	127-18-4	5.0E-02	5.0E-03
VOC/CLP	2-Hexanone	591-78-6	2.0E+00	1.0E-02
VOC/CLP	Dibromochloromethane	124-48-1	5.0E102	5.0E-03
VOC/CLP	1,2-Dibromoethane	106-93-4	5.0E-02	5.0E-03
VOC/CLP	Chlorobenzene	108-90-7	5.0E-02	5.0E-03
VOC/CLP	Ethylbenzene	100-41-4	5.0E-02	5.0E-03
VOC/CLP	o-Xylene	95-47-6	5.0E-02	5.0E-03
VOC/CLP	m,p-Xylene	179601-23-1	5.0E-02	5.0E-03
VOC/CLP	Styrene	100-42-5	5.0E-02	5.0E-03
VOC/CLP	Bromoform	75-25-2	5.0E-02	5.0E-03
VOC/CLP	Isopropylbenzene	98-82-8	2.0E+00	5.0E-03
VOC/CLP	1,1,2,2-Tetrachloroethane	79-34-5	5.0E-02	5.0E-03
VOC/CLP	1,3-Dichlorobenzene	541-73-1	5.0E-02	5.0E-03
VOC/CLP	1,4-Dichlorobenzene	106-46-7	5.0E-02	5.0E-03
VOC/CLP	1,2-Dichlorobenzene	95-50-1	5.0E-02	5.0E-03
VOC/CLP	1,2-Dibromo-3-chloropropane	96-12-8	5.6E-03	5.0E-03
VOC/CLP	1,2,4-Trichlorobenzene	120-82-1	2.0E-01	5.0E-03
VOC/CLP	1,2,3-Trichlorobenzene	87-61-6	NC	5.0E-03

QAPP WORKSHEET #15 CONTINUED
REFERENCE LIMITS AND EVALUATION TABLE

Analytical Group	Analyte	CAS Number	Project Action Limit - Soil (mg/kg)[1]	CRQL - Soil (mg/kg)[2]
SVOC/CLP	Benzaldehyde	100-52-7	7.8E+03	1.7E-01
SVOC/CLP	Phenol	108-95-2	3.3E-01	1.7E-01
SVOC/CLP	bis (2-Chloroethyl) ether	111-44-4	3.3E-01	1.7E-01
SVOC/CLP	2-Chlorophenol	95-57-8	3.3E-01	1.7E-01
SVOC/CLP	2-Methylphenol	95-48-7	3.3E-01	1.7E-01
SVOC/CLP	2,2'-Oxybis(1-chloropropane)	108-60-1	3.5E+00	1.7E-01
SVOC/CLP	Acetophenone	98-86-2	7.8E+03	1.7E-01
SVOC/CLP	4-Methylphenol	106-44-5	3.3E-01	1.7E-01
SVOC/CLP	N-Nitroso-di-n propylamine	621-64-7	3.3E-01	1.7E-01
SVOC/CLP	Hexachloroethane	67-72-1	3.3E-01	1.7E-01
SVOC/CLP	Nitrobenzene	98-95-3	3.3E-01	1.7E-01
SVOC/CLP	Isophorone	78-59-1	3.3E-01	1.7E-01
SVOC/CLP	2-Nitrophenol	88-75-5	3.3E-01	1.7E-01
SVOC/CLP	2,4-Dimethylphenol	105-67-9	3.3E-01	1.7E-01
SVOC/CLP	bis(2-Chloroethoxy) methane	111-91-1	3.3E-01	1.7E-01
SVOC/CLP	2,4-Dichlorophenol	120-83-2	3.3E-01	1.7E-01
SVOC/CLP	Naphthalene	91-20-3	3.3E-01	1.7E-01
SVOC/CLP	4-Chloroaniline	106-47-8	2.4E+02	1.7E-01
SVOC/CLP	Hexachlorobutadiene	87-68-3	3.3E-01	1.7E-01
SVOC/CLP	Caprolactam	105-60-2	3.1E+04	1.7E-01
SVOC/CLP	4-Chloro-3-methylphenol	59-50-7	3.3E-01	1.7E-01
SVOC/CLP	2-Methylnaphthalene	91-57-6	3.3E-01	1.7E-01
SVOC/CLP	Hexachlorocyclopentadiene	77-47-4	3.3E-01	1.7E-01
SVOC/CLP	2,4,6-Trichlorophenol	88-06-2	3.3E-01	1.7E-01
SVOC/CLP	2,4,5-Trichlorophenol	95-95-4	3.3E-01	1.7E-01
SVOC/CLP	1,1-Biphenyl	92-52-4	3.9E+03	1.7E-01
SVOC/CLP	2-Chloronaphthalene	91-58-7	6.3E+03	1.7E-01
SVOC/CLP	2-Nitroaniline	88-74-4	3.3E-01	3.3E-01
SVOC/CLP	Dimethylphthalate	131-11-3	3.3E-01	1.7E-01
SVOC/CLP	2,6-Dinitrotoluene	606-20-2	6.1E+01	1.7E-01
SVOC/CLP	Acenaphthylene	208-96-8	3.3E-01	1.7E-01
SVOC/CLP	3-Nitroaniline	99-09-2	NC	3.3E-01
SVOC/CLP	Acenaphthene	83-32-9	3.3E-01	1.7E-01
SVOC/CLP	2,4-Dinitrophenol	51-28-5	1.2E+02	3.3E-01

QAPP WORKSHEET #15 CONTINUED
REFERENCE LIMITS AND EVALUATION TABLE

Analytical Group	Analyte	CAS Number	Project Action Limit - Soil (mg/kg)[1]	CRQL - Soil (mg/kg)[2]
SVOC/CLP	Dibenzofuran	132-64-9	3.3E-01	1.7E-01
SVOC/CLP	2,4-Dinitrotoluene	121-14-2	3.3E-01	1.7E-01
SVOC/CLP	Diethylphthalate	84-66-2	3.3E-01	1.7E-01
SVOC/CLP	Fluorene	86-73-7	3.3E-01	1.7E-01
SVOC/CLP	4-Chlorophenyl-phenyl ether	7005-72-3	NC	1.7E-01
SVOC/CLP	4-Nitroaniline	100-01-6	NC	3.3E-01
SVOC/CLP	2-Methyl-4,6-dinitrophenol	534-52-1	3.3E-01	3.3E-01
SVOC/CLP	N-Nitrosodiphenylamine	86-30-6	3.3E-01	1.7E-01
SVOC/CLP	1,2,4,5-Tetrachlorobenzene	95-94-3	1.8E+01	1.7E-01
SVOC/CLP	4-Bromophenyl-phenylether	101-55-3	NC	1.7E-01
SVOC/CLP	Hexachlorobenzene	118-74-1	3.3E-01	1.7E-01
SVOC/CLP	Atrazine	1912-24-9	2.1E+00	1.7E-01
SVOC/CLP	Pentachlorophenol	87-86-5	3.3E-01	3.3E-01
SVOC/CLP	Phenanthrene	85-014-8	3.3E-01	1.7E-01
SVOC/CLP	Anthracene	20-12-7	3.3E-01	1.7E-01
SVOC/CLP	Carbazole	86-74-8	3.3E-01	1.7E-01
SVOC/CLP	Di-n-butylphthalate	84-74-2	3.3E-01	1.7E-01
SVOC/CLP	Fluoranthene	206-44-0	3.3E-01	1.7E-01
SVOC/CLP	Pyrene	129-00-0	3.3E-01	1.7E-01
SVOC/CLP	Butylbenzylphthalate	85-68-7	3.3E-01	1.7E-01
SVOC/CLP	3,3'-Dichlorobenzidine	91-94-1	3.3E-01	1.7E-01
SVOC/CLP	Benzo(a)anthracene	56-55-3	3.3E-01	1.7E-01
SVOC/CLP	Benzo(b)fluoranthene	205-99-2	3.3E-01	1.7E-01
SVOC/CLP	Benzo(k)fluoranthene	207-08-9	3.3E-01	1.7E-01
SVOC/CLP	Chrysene	218-01-9	3.3E-01	1.7E-01
SVOC/CLP	bis(2-Ethylhexyl)phthalate	117-81-7	3.3E-01	1.7E-01
SVOC/CLP	Di-n-octylphthalate	117-84-0	3.3E-01	1.7E-01
SVOC/CLP	Benzo(a) pyrene	50-32-8	3.3E-01	1.7E-01
SVOC/CLP	Indeno(1,2,3,-cd)pyrene	193-39-5	3.3E-01	1.7E-01
SVOC/CLP	Dibenzo(a,h)anthracene	53-70-3	3.3E-01	1.7E-01
SVOC/CLP	Benzo(g,h,i) perylene	191-24-2	3.3E-01	1.7E-01
SVOC/CLP	2,3,4,6-Tetrachlorophenol	58-90-2	1.8E+03	1.7E-01

QAPP WORKSHEET #15 CONTINUED
REFERENCE LIMITS AND EVALUATION TABLE

Analytical Group	Analyte	CAS Number	Project Action Limit - Soil (mg/kg)[1]	CRQL - Soil (mg/kg)[2]
PCB/CLP	Aroclor-1016	12674-11-2	1.0E-02	3.3E-02
PCB/CLP	Aroclor-1221	11104-28-2	2.0E-02	3.3E-02
PCB/CLP	Aroclor-1232	11141-16-5	1.0E-02	3.3E-02
PCB/CLP	Aroclor-1242	53469-21-9	1.0E-02	3.3E-02
PCB/CLP	Aroclor-1248	12672-29-6	1.0E-02	3.3E-02
PCB/CLP	Aroclor-1254	11097-69-1	1.0E-02	3.3E-02
PCB/CLP	Aroclor-1260	11096-82-5	1.0E-02	3.3E-02
PCB/CLP	Aroclor-1268	11100-14-4	2.2E-01	3.3E-02
Metals	Aluminum	7429-90-5	5.0E-01	1.8E+00
Metals	Antimony	7440-36-0	5.0E-02	3.7E-02
Metals	Arsenic	7440-38-2	5.0E-02	3.0E-02
Metals	Barium	7440-39-3	5.0E-02	2.8E-01
Metals	Beryllium	7440-41-7	5.0E-02	2.6E-02
Metals	Cadmium	7440-43-9	5.0E-02	5.3E-03
Metals	Calcium	17852-99-2	NC	5.0E+02
Metals	Chromium	7440-47-3	5.0E-02	4.5E-02
Metals	Cobalt	7440-48-4	5.0E-02	1.7E-02
Metals	Copper	7440-50-8	5.0E-02	4.3E-02
Metals	Iron	7439-89-6	5.0E-01	4.7E-01
Metals	Lead	7439-92-1	5.0E-02	4.9E-02
Metals	Magnesium	7439-95-4	5.0E+00	4.4E+00
Metals	Manganese	7439-96-5	5.0E-02	2.1E-01
Metals	Mercury	7439-97-6	2.0E+00	8.0E-03
Metals	Nickel	7440-02-0	5.0E-02	8.1E-01
Metals	Potassium	7440-22-4	NC	5.0E+02
Metals	Selenium	7782-49-2	5.0E-02	4.9E-02
Metals	Silver	7440-22-4	5.0E-02	1.1E-02
Metals	Sodium	7440-23-5	5.0E+00	5.0E+02
Metals	Thallium	7440-28-0	5.0E-02	6.1E-03
Metals	Vanadium	7440-62-2	5.0E-02	3.2E-02
Metals	Zinc	7440-66-6	5.0E-01	4.4E-01
Cyanide	Cyanide	74-90-8	4.0E-01	6.7E-01

QAPP WORKSHEET #15 CONTINUED
REFERENCE LIMITS AND EVALUATION TABLE

Notes:

CAS	Chemical Abstract Services
CLP	Contract Laboratory Program
CRQL	Contract-required quantitation limit
mg/kg	Milligrams per kilogram
NC	No criteria
PCB	Polychlorinated biphenyl
VOC	Volatile organic compound

1 Quantitation limits or reporting limits, as appropriate, listed in the corresponding table in the QAPP (September 2009 revision CRA 2009a) of the PRP. If none are provided, the listed limits are the residential values from the U.S. EPA Regional Screening Levels for Chemical Contaminants at Superfund Sites, September 2008.

2 Laboratory detection limit for non-CLP analyses (metals and cyanide)

Reference Limits Table –Water

Analytical Group	Analyte	CAS Number	Project Action Limit – Water (µg/L)[1]	CRQL - Water (µg/L)[3]
VOC/CLP	Dichlorodifluoromethane	75-71-8	5.0E-01	5.0E+00
VOC/CLP	Chloromethane	74-87-3	5.0E-01	5.0E+00
VOC/CLP	Vinyl chloride	75-01-4	5.0E-01	5.0E+00
VOC/CLP	Bromomethane	74-83-9	5.0E-01	5.0E+00
VOC/CLP	Chloroethane	75-00-3	5.0E-01	5.0E+00
VOC/CLP	Trichlorofluoromethane	75-69-4	5.0E-01	5.0E+00
VOC/CLP	1,1-Dichloroethene	75-35-4	5.0E-01	5.0E+00
VOC/CLP	1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	5.9E+04	5.0E+00
VOC/CLP	Acetone	67-64-1	5.0E+00	1.0E+01
VOC/CLP	Carbon disulfide	75-15-0	5.0E-01	5.0E+00
VOC/CLP	Methyl acetate	79-20-9	3.7E+04	5.0E+00
VOC/CLP	Methylene chloride	75-09-2	5.0E-01	5.0E+00
VOC/CLP	trans-1,2-Dichloroethene	156-50-5	5.0E-01	5.0E+00
VOC/CLP	Methyl tert-butyl ether	1634-04-4	5.0E-01	5.0E+00
VOC/CLP	1,1-Dichloroethane	75-34-3	5.0E-01	5.0E+00
VOC/CLP	cis-1,2-Dichloroethene	156-59-2	5.0E-01	5.0E+00
VOC/CLP	2-Butanone	78-93-3	5.0E+00	1.0E+01
VOC/CLP	Bromochloromethane	74-97-5	NC	5.0E+00
VOC/CLP	Chloroform	67-66-3	5.0E-01	5.0E+00
VOC/CLP	1,1,1-Trichloroethane	71-55-6	5.0E-01	5.0E+00
VOC/CLP	Cyclohexane	110-82-7	1.3E+04	5.0E+00
VOC/CLP	Carbon tetrachloride	56-23-5	5.0E-01	5.0E+00
VOC/CLP	Benzene	71-43-2	5.0E-01	5.0E+00
VOC/CLP	1,2-Dichloroethane	107-06-2	5.0E-01	5.0E+00
VOC/CLP	1,4-Dioxane	123-91-1	6.1E+00	1.0E+02
VOC/CLP	Trichloroethene	79-01-6	5.0E-01	5.0E+00
VOC/CLP	Methylcyclohexane	108-87-2	6.3E+03	5.0E+00
VOC/CLP	1,2-Dichloropropane	78-87-5	5.0E-01	5.0E+00
VOC/CLP	Bromodichloromethane	75-27-4	5.0E-01	5.0E+00
VOC/CLP	cis-1,3-Dichloropropene	542-75-6	5.0E-01	5.0E+00

QAPP WORKSHEET #15 CONTINUED
REFERENCE LIMITS AND EVALUATION TABLE

Analytical Group	Analyte	CAS Number	Project Action Limit – Water (µg/L)[1]	CRQL - Water (µg/L)[3]
VOC/CLP	4-Methyl-2-pentanone	108-10-1	5.0E+00	1.0E+01
VOC/CLP	Toluene	108-88-3	5.0E-01	5.0E+00
VOC/CLP	trans-1,3-Dichloropropene	10061-02-6	5.0E-01	5.0E+00
VOC/CLP	1,1,2-Trichloroethane	79-00-5	5.0E-01	5.0E+00
VOC/CLP	Tetrachloroethene	127-18-4	5.0E-01	5.0E+00
VOC/CLP	2-Hexanone	591-78-6	5.0E+00	1.0E+01
VOC/CLP	Dibromochloromethane	124-48-1	5.0E-01	5.0E+00
VOC/CLP	1,2-Dibromoethane	106-93-4	5.0E-01	5.0E+00
VOC/CLP	Chlorobenzene	108-90-7	5.0E-01	5.0E+00
VOC/CLP	Ethylbenzene	100-41-4	5.0E-01	5.0E+00
VOC/CLP	o-Xylene	95-47-6	5.0E-01	5.0E+00
VOC/CLP	m,p-Xylene	179601-23-1	5.0E-01	5.0E+00
VOC/CLP	Styrene	100-42-5	5.0E-01	5.0E+00
VOC/CLP	Bromoform	75-25-2	5.0E-01	5.0E+00
VOC/CLP	1,1,2,2-Tetrachloroethane	79-34-5	5.0E-01	5.0E+00
VOC/CLP	1,3-Dichlorobenzene	541-73-1	5.0E-01	5.0E+00
VOC/CLP	1,4-Dichlorobenzene	106-45-7	5.0E-01	5.0E+00
VOC/CLP	1,2-Dichlorobenzene	95-50-1	5.0E-01	5.0E+00
VOC/CLP	1,2-Dibromo-3-chloropropane	96-12-8	2.0E-01[2]	5.0E+00
VOC/CLP	1,2,4-Trichlorobenzene	120-82-1	5.0E-01	5.0E+00
VOC/CLP	1,2,3-Trichlorobenzene	87-61-6	NC	5.0E+00
SVOC/CLP	Benzaldehyde	100-52-7	1.0E+01	5.0E+00
SVOC/CLP	Phenol	108-95-2	1.0E+01	5.0E+00
SVOC/CLP	bis (2-Chloroethyl) ether	111-44-4	1.0E+01	5.0E+00
SVOC/CLP	2-Chlorophenol	95-57-8	1.0E+01	5.0E+00
SVOC/CLP	2-Methylphenol	95-48-7	1.0E+01	5.0E+00
SVOC/CLP	2,2'-Oxybis(1-chloropropane)	108-60-1	3.2E-01	5.0E+00
SVOC/CLP	4-Methylphenol	106-44-5	1.0E+01	5.0E+00
SVOC/CLP	Acetophenone	98-86-2	3.7E+03	5.0E+00

QAPP WORKSHEET #15 CONTINUED
REFERENCE LIMITS AND EVALUATION TABLE

Analytical Group	Analyte	CAS Number	Project Action Limit – Water (µg/L)[1]	CRQL - Water (µg/L)[3]
SVOC/CLP	N-Nitroso-di-n-propylamine	621-64-7	1.0E+01	5.0E+00
SVOC/CLP	Hexachloroethane	67-72-1	1.0E+01	5.0E+00
SVOC/CLP	Nitrobenzene	98-95-3	1.0E+01	5.0E+00
SVOC/CLP	Isophorone	78-59-1	1.0E+01	5.0E+00
SVOC/CLP	2-Nitrophenol	88-75-5	1.0E+01	5.0E+00
SVOC/CLP	2,4-Dimethylphenol	105-67-9	1.0E+01	5.0E+00
SVOC/CLP	2,4-Dichlorophenol	120-83-2	1.0E+01	5.0E+00
SVOC/CLP	Naphthalene	91-20-3	1.0E+01	5.0E+00
SVOC/CLP	4-Chloroaniline	106-47-8	1.5E+02	5.0E+00
SVOC/CLP	Hexachlorobutadiene	87-68-3	1.0E+01	5.0E+00
SVOC/CLP	Caprolactam	105-60-2	1.8E+04	5.0E+00
SVOC/CLP	4-Chloro-3-methylphenol	59-50-7	1.0E+01	5.0E+00
SVOC/CLP	2-Methylnaphthalene	91-57-6	1.0E+01	5.0E+00
SVOC/CLP	Hexachlorocyclopentadiene	77-47-4	1.0E+01	5.0E+00
SVOC/CLP	2,4,6-Trichlorophenol	88-06-2	1.0E+01	5.0E+00
SVOC/CLP	2,4,5-Trichlorophenol	95-95-4	1.0E+01	5.0E+00
SVOC/CLP	1,1-Biphenyl	92-52-4	1.8E+03	5.0E+00
SVOC/CLP	2-Chloronaphthalene	91-58-7	2.9E+03	5.0E+00
SVOC/CLP	2-Nitroaniline	88-74-4	NC	1.0E+01
SVOC/CLP	4,6-Dinitro-2-methylphenol	534-52-1	NC	1.0E+01
SVOC/CLP	N-Nitrosodiphenylamine	86-30-6	1.0E+01	5.0E+00
SVOC/CLP	1,2,4,5-Tetrachlorobenzene	95-94-3	1.1E+01	5.0E+00
SVOC/CLP	Hexachlorobenzene	118-74-1	1.0E+01	5.0E+00
SVOC/CLP	Dimethylphthalate	131-11-3	1.0E+01	5.0E+00
SVOC/CLP	2,6-Dinitrotoluene	606-20-2	NC	5.0E+00
SVOC/CLP	Acenaphthylene	208-96-8	1.0E+01	5.0E+00
SVOC/CLP	3-Nitroaniline	99-09-2	7.3E+01	1.0E+01
SVOC/CLP	Acenaphthene	83-32-9	1.0E+01	5.0E+00
SVOC/CLP	2,4-Dinitrophenol	51-28-5	1.0E+01	1.0E+01

QAPP WORKSHEET #15 CONTINUED
REFERENCE LIMITS AND EVALUATION TABLE

Analytical Group	Analyte	CAS Number	Project Action Limit – Water (µg/L)[1]	CRQL - Water (µg/L)[3]
SVOC/CLP	4-Nitrophenol	100-02-7	NC	1.0E+01
SVOC/CLP	Dibenzofuran	132-64-9	NC	5.0E+00
SVOC/CLP	2,4-Dinitrotoluene	121-14-2	1.0E+01	5.0E+00
SVOC/CLP	Diethylphthalate	84-66-2	1.0E+01	5.0E+00
SVOC/CLP	Fluorene	86-73-7	1.0E+01	5.0E+00
SVOC/CLP	4-Chlorophenyl-phenyl ether	7005-72-3	NC	5.0E+00
SVOC/CLP	4-Nitroaniline	100-01-6	NC	1.0E+01
SVOC/CLP	Atrazine	1912-24-9	2.9E-01	5.0E+00
SVOC/CLP	Pentachlorophenol	87-86-5	1.0E+01	1.0E+01
SVOC/CLP	Phenanthrene	85-014-8	1.0E+01	5.0E+00
SVOC/CLP	Anthracene	20-12-7	1.0E+01	5.0E+00
SVOC/CLP	Carbazole	86-74-8	3.4E+00	5.0E+00
SVOC/CLP	Di-n-butylphthalate	84-74-2	1.0E+01	5.0E+00
SVOC/CLP	Fluoranthene	206-44-0	1.0E+01	5.0E+00
SVOC/CLP	Pyrene	129-00-0	1.0E+01	5.0E+00
SVOC/CLP	Butylbenzylphthalate	85-68-7	1.0E+01	5.0E+00
SVOC/CLP	3,3'-Dichlorobenzidine	91-94-1	1.0E+01	5.0E+00
SVOC/CLP	Benzo(a)anthracene	56-55-3	1.0E+01	5.0E+00
SVOC/CLP	Chrysene	218-01-9	1.0E+01	5.0E+00
SVOC/CLP	bis (2-Ethylhexyl) phthalate	117-81-7	1.0E+01	5.0E+00
SVOC/CLP	Di-n-octylphthalate	117-84-0	1.0E+01	5.0E+00
SVOC/CLP	Benzo(b)fluoranthene	205-99-2	1.0E+01	5.0E+00
SVOC/CLP	Benzo(k)fluoranthene	207-08-9	1.0E+01	5.0E+00
SVOC/CLP	Benzo(a)pyrene	50-32-8	1.0E+01	5.0E+00
SVOC/CLP	Indeno(1,2,3,-cd) pyrene	193-39-5	1.0E+01	5.0E+00
SVOC/CLP	Dibenzo(a,h) anthracene	53-70-3	1.0E+01	5.0E+00
SVOC/CLP	Benzo(g,h,i)perylene	191-24-2	1.0E+01	5.0E+00
SVOC/CLP	2,3,4,6-Tetrachlorophenol	58-90-03	1.1E+03	5.0E+00

QAPP WORKSHEET #15 CONTINUED
REFERENCE LIMITS AND EVALUATION TABLE

Analytical Group	Analyte	CAS Number	Project Action Limit – Water (µg/L)[1]	CRQL - Water (µg/L)[3]
PCB/CLP	Aroclor-1016	12674-11-2	2.0E-01	1.0E+00
PCB/CLP	Aroclor-1221	11104-28-2	2.0E-01	1.0E+00
PCB/CLP	Aroclor-1232	11141-16-5	2.0E-01	1.0E+00
PCB/CLP	Aroclor-1242	53469-21-9	2.0E-01	1.0E+00
PCB/CLP	Aroclor-1248	12672-29-6	2.0E-01	1.0E+00
PCB/CLP	Aroclor-1254	11097-69-1	2.0E-01	1.0E+00
PCB/CLP	Aroclor-1260	11096-82-5	2.0E-01	1.0E+00
PCB/CLP	Aroclor-1268	11100-14-4	3.4E-02	1.0E+00
Metals	Aluminum	7429-90-5	5.0E+00	2.4E+01
Metals	Antimony	7440-36-0	5.0E-01	4.0E-01
Metals	Arsenic	7440-38-2	5.0E-01	3.9E-01
Metals	Barium	7440-39-3	5.0E-01	2.8E-01
Metals	Beryllium	7440-41-7	5.0E-01	3.1E-01
Metals	Cadmium	7440-43-9	5.0E-01	6.0E-02
Metals	Calcium	17852-99-2	NC	5.0E+03
Metals	Chromium	7440-47-3	5.0E-01	3.4E-01
Metals	Cobalt	7440-48-4	5.0E-01	3.6E-02
Metals	Copper	7440-50-8	5.0E-01	2.6E-01
Metals	Iron	7439-89-6	5.0E-01	8.0E+00
Metals	Lead	7439-92-1	5.0E-01	2.6E-01
Metals	Magnesium	7439-95-4	5.0E+02	4.4E+01
Metals	Manganese	7439-96-5	5.0E-01	2.4E101
Metals	Mercury	7439-97-6	1.0E-.3	5.0E-04
Metals	Nickel	7440-02-0	5.0E-01	4.2E+00
Metals	Potassium	7440-22-4	NC	5.0E+03
Metals	Selenium	7782-49-2	5.0E-01	4.0E-01
Metals	Silver	7440-22-4	5.0E-01	5.3E-02
Metals	Sodium	7440-23-5	5.0E+01	8.2E+01

QAPP WORKSHEET #15 CONTINUED
REFERENCE LIMITS AND EVALUATION TABLE

Analytical Group	Analyte	CAS Number	Project Action Limit – Water (µg/L)[1]	CRQL - Water (µg/L)[3]
Metals	Thallium	7440-28-0	5.0E-01	5.0E-02
Metals	Vanadium	7440-62-2	5.0E-01	3.0E-01
Metals	Zinc	7440-66-6	5.0E+00	2.0E+00
Cyanide	Cyanide	57-12-5	9.0E+00	2.3E+00

Notes:
µg/L Microgram per liter
CAS Chemical Abstract Services
CLP Contract Laboratory Program
CRQL Contract-required quantitation limit
NC No criteria
PCB Polychlorinated biphenyl
VOC Volatile organic compound

1 Quantitation limits or reporting limits, as appropriate, listed in the corresponding table of the QAPP (September 2009 revision CRA 2009a) of the PRP. If none are provided, the listed limits are drinking water values from the U.S. EPA Regional Screening Levels for Chemical Contaminants at Superfund Sites, September 2008.

3 Laboratory detection limit for non-CLP analyses (metals and cyanide).

QAPP WORKSHEET #16
PROJECT SCHEDULE/TIMELINE TABLE

(UFP QAPP Section 2.8.2)
List all project activities as well as the QA assessments that will be performed during the course of the project. Include the anticipated start and completion dates.

Activity	Organization	Date		Deliverable	Deliverable Due Date
		Anticipated Date of Initiation	Anticipated Date of Completion[3]		
Field sampling[1]	SulTRAC	November 2009	March 2010	Periodic (Weekly) Oversight Report	5 business days after each weekly sampling event
Field sampling[1]	SulTRAC	November 2009	March 2010	Final Summary Report	28 days after the end of all RI/FS field activities
Data validation[2]	SulTRAC	February 2010	March 2010	Data Validation Letter Report	21 days after receipt of laboratory data package
Data evaluation[2]	SulTRAC	March 2010	March 2010	Data Evaluation Summary Report	45 days after receipt of CLP-validated data and PRP data

Note:

1 At the Plainwell Mill site, the schedule is determined by the PRP, possibly in consultation with EPA.

2 Data validation will be conducted by EPA after each sampling event. SulTRAC will review data validation results upon arrival of the results and will submit one data evaluation summary report to EPA presenting a comparison of SulTRAC's and the PRP's split sample analytical data at the end of the investigation. In addition, SulTRAC will perform data validation on the special analytical services required from a commercial laboratory.

3 Additional sampling expected to be completed in March 2010, although unforeseen delays could extend completion to March 2011 at the latest.

QAPP WORKSHEET #17
SAMPLING DESIGN AND RATIONALE

(UFP QAPP Section 3.1.1)
Describe the project sampling approach. Provide the rationale for selecting sample locations and matrices for each analytical group and concentration level.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be collected, and the sampling frequency (including seasonal considerations). (May refer to map or Worksheet #18 for details).

During RI/FS activities at Plainwell Mill site, SulTRAC will collect split samples from 25% of the PRP's 400 soil and 50 water samples. Therefore, SulTRAC will collect 81 soil and approximately 11 water split samples. The split samples will be analyzed for VOCs, SVOCs*, and PCBs by a CLP laboratory; for metals, cyanide, low-level mercury, SPLP metals and SPLP cyanide by TriMatrix Laboratories. In addition to the split samples, QA/QC samples for each analytical method will be collected at a frequency of one field duplicate for every 10 samples, one matrix spike and matrix spike duplicate for every 20 samples, and one trip blank for every VOC sample shipment to the laboratory. An estimated total of 24 QA/QC samples will be collected based on the above formula.

Based on the PRP's FSP (RMT 2008a), sample matrices, locations, expected concentrations, and sampling frequencies for the Plainwell Mill site will be determined in the field. Therefore, SulTRAC will use the above information, as well as field observations, to select locations for collecting split samples.

Note:

* SulTRAC will sample for SVOCs instead of the PAHs per CLP methods and at the request of the EPA WAM.

QAPP WORKSHEET #18
SAMPLING LOCATIONS/IDS, SAMPLE DEPTHS, SAMPLE ANALYSES AND SAMPLING PROCEDURES TABLE

(UFP QAPP Section 3.1.1)
List all locations that will be sampled indicating the sample identity (ID) number or sample location. Specify sample matrix and depth at which samples will be taken. List all analyses the samples will be analyzed for.
Specify the appropriate SOP or specific section in the SAP that describes the sample collection procedure.

Sampling Location[1]/ ID Number	Matrix	Depth (feet bgs)	Analytical Group	Sampling SOP Reference[2]
TBD	Soil/Sediment	NA	CLP SOW SOM01.2 (VOCs, SVOCs, and PCBs) Metals and Cyanide by SW-846 Methods	S-1, S-2, S-3
TBD	Water	NA	CLP SOW SOM01.2 (VOCs, SVOCs, and PCBs) Metals and Cyanide by SW-846 Methods	S-4, S-5

Notes:

bgs Below ground surface
NA Not applicable
SOP Standard operating procedure
TBD To be determined

1 Split samples will be collected from soil, sediment, surface water, and groundwater.
2 The PRP will be conducting the sampling; therefore, the PRP will use its own SOPs. The PRP's SOPs are found in the Appendix following the FSP (RMT 2008a). See Worksheet #21 for a list of PRP sample collection SOPs and sampling-related SOPs that SulTRAC will use to package samples and record field observations.

QAPP WORKSHEET #19
ANALYTICAL METHODS, CONTAINERS, PRESERVATIVES, AND HOLDING TIMES TABLE

(UFP QAPP Section 3.1.1)
For each matrix and analytical group list the analytical and preparation method and associated container specifications, preservation requirements, and maximum holding time.

Matrix	Analytical Group	Analytical and Preparation Method	Containers (number, size, type)	Preservation Requirements (chemical, temperature, etc.)	Maximum Holding Time (preparation/analysis)[1]
Soil	VOCs	CLP SOW SOM01.2	Three 40-mL glass containers with PTFE-lined septa and open-top screw caps, pre-weighed and containing magnetic stir bars and one container of sample filled with no headspace for determination of moisture content or At least three coring tools used as transport devices (for example, 5-gram samplers) and one container of sample filled with no head space for determination of moisture content	Cool to 4 °C ± 2 °C immediately after collection or Frozen (-7 ºC to -15 ºC)	48 hours to preservation at laboratory/14 days for analysis following preservation or 48 hours (frozen) to preservation at laboratory for analysis after preservation
Soil	SVOCs	CLP SOW SOM01.2	Two 4-ounce, wide-mouth glass jars	Cool to 4 °C ± 2 °C immediately after collection	14 days/40 days
Soil	PCBs	CLP SOW SOM01.2	Two 4-ounce, wide-mouth glass jars	Cool to 4 °C ± 2 °C immediately after collection	14 days/40 days
Soil	Metals	SW-846 Methods 6010B/6020A and 7471A	One 8-ounce, wide-mouth glass jar	Cool to 4 °C ± 2 °C immediately after collection	6 months (28 days for mercury)
Soil	Cyanide	SW-846 Method 9010B/9014	One 8-ounce, wide-mouth glass jar	Cool to 4 °C ± 2 °C immediately after collection	14 days
Soil	SPLP extraction	SW-846 Method 1312	One 8-ounce, wide-mouth glass jar	Cool to 4 °C ± 2 °C immediately after collection	14 days

QAPP WORKSHEET #19 (CONTINUED)
ANALYTICAL METHODS, CONTAINERS, PRESERVATIVES, AND HOLDING TIMES TABLE

Matrix	Analytical Group	Analytical and Preparation Method	Containers (number, size, type)	Preservation Requirements (chemical, temperature, etc.)	Maximum Holding Time (preparation/analysis) [1]
Water	VOCs	CLP SOW SOM01.2	Three 40-mL glass vials with PTFE-lined septa and open-top screw caps	No headspace Cool to 4 ºC ± 2 ºC Adjust pH to less than 2 with HCl	14 days
Water	SVOCs	CLP SOW SOM01.2	Two 1-liter amber glass bottles fitted with PTFE-lined screw caps	Cool to 4 °C ± 2 °C immediately after collection; keep away from light	7 days/40 days
Water	PCBs	CLP SOW SOM01.2	Two 1-liter amber glass bottles fitted with PTFE-lined screw caps	Cool to 4 °C ± 2 °C immediately after collection; keep away from light	7 days/40 days
Water	Metals	SW-846 Methods 6020 and 1631	One 1-liter high-density polyethylene bottle	Acidify to pH < 2 with HNO_3 and cool to 4 C (±2 C) immediately after collection	6 months (28 days for mercury)
Water	Cyanide	SW-846 Method 9014	One 1-liter high-density polyethylene bottle	Alkalinize to pH > 12 with NaOH and cool to 4 C (±2 C) immediately after collection	14 days

Notes:

ºC Degrees Celsius
CLP Contract Laboratory Program
HCl Hydrochloric acid
HNO_3 Nitric acid
mL Milliliter
NA Not applicable
PCB Polychlorinated biphenyl
PTFE Polytetrafluoroethylene
SOW Statement of work
SPLP Synthetic precipitation leaching procedure
VOC Volatile organic compound

1 Holding time is applicable from validated time of sample receipt and is measured to time of sample extraction and analysis.

QAPP WORKSHEET #20
FIELD QUALITY CONTROL SAMPLE SUMMARY TABLE

(UFP QAPP Section 3.1.1)
Summarize by matrix and analytical group.

Matrix	Analytical Group	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations	No. of Samples	No. of Field Duplicates[2]	No. of MS/MSDs[3]	No. of Trip Blanks[4]	Total No. of Samples to Laboratory
Soil/Sediment and Water	CLP VOCs, SVOCs, and PCBs; non-CLP Metals and Cyanide	A-1, A-2	NA	113	12	6	6	137

Notes:

1 Analytical and preparation SOPs are listed in Worksheet #23.
2 Field duplicates are collected at a rate of 1 per 10 investigative samples of the same matrix.
3 MS/MSD samples are collected at a rate of 1 per 20 investigative samples of the same matrix.
4 A trip blank will be provided with each shipping container with samples to be analyzed for VOCs.

QAPP WORKSHEET #21
PROJECT SAMPLING SOP REFERENCES TABLE

(UFP Section 3.1.2)
List all SOPs associated with project sampling including, but not limited to, sample collection, sample preservation, equipment cleaning and decontamination, equipment testing, inspection and maintenance, supply inspection and acceptance, and sample handling and custody. Include copies of the SOPs as attachments or reference all in the QAPP. Sequentially number sampling SOP references in the Reference Number column. The reference number can be used throughout the QAPP to refer to a specific SOP.

Reference Number	Title, Revision, Date and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
S-1	SOP F-4, Sediment Sampling	RMT, Inc.	Spatula, spade or shove, scoop, bucket or tube auger, sediment coring device, or Ponar or Ekman dredge	N	None
S-2	SOP F-6, Surficial Soil Sampling	RMT, Inc.	Spoon or spatulas, trowel, scoop	N	None
S-3	SOP F-8, Excavation of Test Pits and Test Pit Soil Sampling	RMT, Inc.	PID, Ziploc bags, spatula, stainless steel scoop, plastic or steel spoons, trowel	N	None
S-4	SOP F-1, Water Sampling and Field Measurement Procedures	RMT Inc.	Kemmerer water sampler, peristaltic pump, or ISCO automated sampler	N	None
S-5	SOP F-11, Groundwater Sampling and Field Measurement Procedures	RMT Inc.	Pumps, flow-through cell, water quality meter	N	None
S-6	Packaging and Shipping Samples, December 2008, SOP 019-6	SulTRAC	Coolers, ice, bubble wrap or similar cushioning material, COC forms, airbills, resealable plastic bags for sample jars, ice, and tape	N	None
S-7	Recording of Notes in Field Logbook December 2008, SOP 024-1	SulTRAC	Field logbooks, ballpoint pens with permanent ink, 6-inch ruler (optional)	N	None

Notes:

COC Chain of custody
PID Photoionization detector
SOP Standard Operating Procedure

QAPP WORKSHEET #22
FIELD EQUIPMENT CALIBRATION, MAINTENANCE, TESTING, AND INSPECTION TABLE

(UFP QAPP Section 3.1.2.4)

Identify all field equipment/instruments that require calibration, maintenance, testing, or inspection activities. Specify the frequency of each activity, acceptance criteria, and corrective action requirements. Provide the SOP reference number for each type of equipment, if available.

Field Equipment	Calibration Activity[1]	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference	Comments
NA	NA	NA	NA	NA	NA	NA	See note below

Notes:

NA Not applicable

[1] SulTRAC's field activities are limited to collecting split samples and do not include field measurements. However, SulTRAC will oversee field measurements by the PRP.

QAPP WORKSHEET #23
ANALYTICAL SOP REFERENCES TABLE

(UFP QAPP Section 3.2.1)
List all SOPs that will be used to perform on-site or off-site analysis. Indicate whether the procedure produces screening or definitive data. Sequentially number analytical SOP references in the reference number column. The reference number can be used throughout the QAPP to refer to a specific SOP. Include copies of the SOPs as attachments or reference in the QAPP.

Reference Number	Title, Revision, Date, and/or Number	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work?
A-1	CLP SOW SOM01.2 for Organics Analysis, Multi-Media, Multi-Concentration	Definitive	VOCs, SVOCs	GC/mass spectroscopy	CLP Laboratory	No
A-1	CLP SOW SOM01.2 for Organics Analysis, Multi-Media, Multi-Concentration	Definitive	PCBs	GC/electron capture detector	CLP Laboratory	No
A-2	Current editions (reviewed annually, revised as necessary) of laboratory SOPs for stated methods and incorporated sample preparation techniques.	Definitive	Metals and Cyanide	ICP/AES ICP/MS Cold vapor atomic absorption UV Spectrophotometry	TriMatrix Laboratories, Inc.	No

Notes:

AES Atomic emission spectroscopy
CLP Contract Laboratory Program
GC Gas chromatograph
ICP Inductively coupled plasma
MS Mass spectroscopy
PCB Polychlorinated biphenyl
SOW Statement of work
SVOC Semi-volatile organic compound
VOC Volatile organic compound
UV Ultra-violet

QAPP WORKSHEET #24
ANALYTICAL INSTRUMENT CALIBRATION TABLE

(UFP Section 3.2.2)

Identify all analytical instrumentation that requires calibration and provide the SOP reference number for each. In addition, document the frequency, acceptance criteria, and corrective action requirements on the worksheet.

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
GC/Mass Spectroscopy (Soil & Water analysis)	VOCs and SVOCs: Run five calibration standard solutions and a blank	12-hour continuing calibration acceptance criteria	Always, RRF ≥ 0.050 or per SOP Initial, RSD ≤ 20% or 40%, depending on compound. Continuing, %D ≤ 25% or 40% depending on compound for opening and ≤ 50% for closing.	Inspect the system for problems, clean the ion source, change the column, service the purge and trap device, and take corrective actions to achieve the technical acceptance criteria.	CLP Laboratory Analyst	A-1
GC/Electron Capture Detector	PCBs: Run five calibration standard solutions and a blank	12-hour continuing calibration acceptance criteria	Always, resolution per SOP Initial, CF RSD ≤ 20% Continuing, CF %D ≤ 15 for opening and ≤ 50 for closing	Inspect the system for problems, change the column, bake out the detector, clean the injection port, and take other corrective actions to achieve the acceptance criteria.	CLP Laboratory Analyst	A-1
ICP/AES, ICP/MS	Run four (ICP/AES) or seven (ICP/MS) calibration mixed standard solutions and a blank	Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV)	Deviation from the initial calibration verification: metals 90-110%	Inspect the system for problems, clean the system, verify operating conditions, and take CAs to achieve the technical acceptance criteria.	TriMatrix Laboratories, Inc. Analyst	A-2

QAPP WORKSHEET #24 (CONTINUED)
ANALYTICAL INSTRUMENT CALIBRATION TABLE

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
Cold Vapor Atomic Absorption	Run five calibration mixed standard solutions and a blank	Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV)	Deviation from the initial calibration verification: metals 90-110% (Method 7471A) or 77-123% (Method 1631)	Inspect the system for problems, clean the system, verify operating conditions, and take CAs to achieve the technical acceptance criteria.	TriMatrix Laboratories, Inc. Analyst	A-2
UV Spectrophotometry	Run six calibration mixed standard solutions and a blank	Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV)	Deviation from the initial calibration verification: metals 90-110%	Inspect the system for problems, clean the system, verify operating conditions, and take CAs to achieve the technical acceptance criteria.	TriMatrix Laboratories, Inc. Analyst	A-2

Notes:
[1] Analytical and preparation SOPs are listed in Worksheet #23

%D Percent difference
AES Atomic emission spectroscopy
CA Corrective action
CCV Continuing calibration verification
CLP Contract laboratory program
CF Calibration factor
GC Gas Chromatograph
ICP Inductively coupled plasma
MS Mass Spectroscopy
RRF Relative response factor
RSD Relative standard deviation
SOP Standard operating procedures
UV Ultraviolet
VOC Volatile organic compounds

QAPP WORKSHEET #25
ANALYTICAL INSTRUMENT AND EQUIPMENT MAINTENANCE TESTING, AND INSPECTION TABLE

(UFP QAPP Section 3.2.2)
Identify all analytical instrumentation that requires maintenance, testing, or inspection and provide the SOP reference number for each. In addition, document the frequency, acceptance criteria, and corrective action requirements on the worksheet.

Instrument/ Equipment	Maintenance Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action (CA)	Responsible Person	SOP Reference[1]
GC/Mass Spectroscopy	Daily Check, Instrument tune (4-bromofluorobenzene or decafluorotriphenylphosphine)	Injector syringe, injector septum, injector liner/seal, injector port, guard column, column splitter, analytical column, ion source, detector, traps, and gas supply	See A-1	See A-1	Inspect the system for problems, clean the ion source, change the column, and service the purge and trap device.	CLP Laboratory Analyst	A-1
GC/Electron Capture Detector	Daily Check, Initial Calibration Verification	Injector syringe, injector septum, injector liner/seal, injector port, guard column, column splitter, analytical column, ion source, detector, traps, and gas supply	See A-1	See A-1	Inspect the system for problems, change the column, bake out the detector, and clean the injection port.	CLP Laboratory Analyst	A-1
ICP/AES, ICP/MS	Daily Check, Initial Calibration Verification	Nebulizer, injection tube, flame optimization, gas supply, and detector	See A-2	See A-2	Inspect the system for problems, clean the system, verify operating conditions, and take corrective actions to achieve the technical acceptance criteria.	TriMatrix Laboratories, Inc. Analyst	A-2
Spectrophotometer	Daily Check, Initial Calibration Verification	Tubing, pumps, reagent supplies, plus instrument self-check	See A-2	See A-2	Inspect the system for problems, clean the system, verify operating conditions, and take corrective actions to achieve the technical acceptance criteria.	TriMatrix Laboratories, Inc. Analyst	A-2

Notes:
AES Atomic emission spectroscopy
CLP Contract laboratory program
GC Gas chromatography
ICP Inductively coupled plasma
MS Mass spectroscopy

1 See Worksheet #23 for identification of analytical methods.

QAPP WORKSHEET #26
SAMPLE HANDLING SYSTEM

(UFP QAPP Appendix A)
Record personnel, and their organizational affiliations, who are primarily responsible for ensuring proper handling, custody, and storage of field samples from the time of collection, to laboratory delivery, to final sample disposal. Indicate the number of days field samples and their extracts/digestates will be archived prior to disposal.

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): Field sampling personnel/SulTRAC
Sample Packaging (Personnel/Organization): Field sampling personnel/SulTRAC
Coordination of Shipment (Personnel/Organization): Field sampling personnel/SulTRAC
Type of Shipment/Carrier: Cooler packed with ice and packing material such as bubble wrap/FedEx or other overnight courier
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Laboratory personnel/CLP laboratory
Sample Custody and Storage (Personnel/Organization): Laboratory personnel/CLP laboratory
Sample Preparation (Personnel/Organization): Laboratory personnel/CLP laboratory
Sample Determinative Analysis (Personnel/Organization): Laboratory personnel/CLP laboratory
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): See Worksheet # 27
SAMPLE DISPOSAL
Personnel/Organization: Laboratory personnel/CLP laboratory
Number of Days from Analysis: TBD (or in accordance with individual laboratory SOP)

Notes:

CLP Contract laboratory program
SOP Standard operating procedure
TBD To be determined

QAPP WORKSHEET #27
SAMPLE CUSTODY REQUIREMENTS

(UFP Appendix A)
Describe the procedures that will be used to maintain sample custody and integrity. Include examples of chain of custody forms, traffic reports, sample identification, custody seals, laboratory sample receipt forms, and laboratory sample transfer forms. Attach or reference applicable SOPs.

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to the laboratory): SulTRAC will use EPA's Field Operations and Records Management System (FORMS II Lite) software to manage sample collection, documentation, chain of custody, and reporting. Field personnel will input data into FORMS II Lite and then use the software to generate sample labels, bottle tags, and chain-of-custody forms to track samples from the field to the laboratory. Because FORMS II Lite captures sample management information electronically, the information is easily exportable to databases or various reporting formats.

Chain-of-custody forms will be signed in ink by the samplers and the individual relinquishing custody. SulTRAC will then follow the sample packaging and shipment procedures summarized below to ensure that samples arrive at the laboratory with the chain of custody intact.

1- Immediately after sample collection, sample containers will be labeled with the appropriate identifiers. Clear tape will be placed over the sample container's labels to prevent smearing.

2- The samples will be placed in Ziploc plastic bags and then in a cooler containing double-sealed bags of ice and maintained at 4 ^{o}C. The cooler will remain in a secured area or in view of the sampler until it is properly sealed for shipment to the laboratory.

3- Prior to shipping, the chain-of-custody forms, airbills, and all other relevant documents will be completed. Chain-of-custody forms will be sealed in plastic bags and taped to the inside of the cooler lid. Cushioning material, such as bubble-wrap, will be placed in the cooler.

4- A temperature blank consisting of a jar or vial containing water will be included in every cooler. The temperature blank will be used by the laboratory to determine the cooler temperature at the time of sample receipt.

5- The shipping cooler will then be sealed with tape and custody seals in a manner that will indicate whether the cooler was opened. The preferred procedure includes placement of custody seals at diagonally opposite corners of the cooler. The custody seals will be covered with clear plastic tape or strapping tape.

The field sampler is personally responsible for the care and custody of the samples until they are transferred to other personnel or properly dispatched to an overnight carrier or directly to a laboratory. When transferring possession of the samples, the individuals relinquishing and receiving the samples sign, date, and note the time of transfer on the chain-of-custody form. Commercial carriers are not required to sign off on the chain-of-custody form as long as the form is sealed inside the sample cooler and the custody seals remain intact.

QAPP WORKSHEET #27 (CONTINUED)
SAMPLE CUSTODY REQUIREMENTS

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal): The laboratory sample custodian will receive all incoming samples and indicate receipt by signing the accompanying custody forms and retaining copies of the signed forms as permanent records. The laboratory sample custodian will record all pertinent information concerning the sample, including the persons delivering and receiving the sample, the date and time received, the method by which the sample was transmitted to the laboratory, sample condition at the time of receipt (sealed, unsealed, or broken container; temperature; or other relevant remarks), the sample identification number, and any unique laboratory identification number associated with the sample. This information should be entered into a computerized laboratory information management system (LIMS).

The laboratory will provide a secure storage area, restricted to authorized personnel, for all samples. Only the custodian can distribute samples to laboratory personnel authorized to conduct the required analyses. Laboratory analytical personnel are responsible for the care and custody of the sample upon receipt.

At the completion of sample analysis, any unused portion of the sample, together with all identifying labels, will be returned to the custodian. The returned sample will be retained in secure storage until the custodian receives permission to dispose of the sample. Sample disposal will occur only on the order of the laboratory project manager in consultation with EPA or SulTRAC, or when it is certain that the information is no longer required or the samples have deteriorated. Likewise, laboratory records will be maintained until the information is no longer required and final disposition is ordered by the laboratory project manager in consultation with EPA or SulTRAC.

Sample Identification Procedures: Sample identification will be as described in Section 8.2 of the FSP (SulTRAC 2009). Each sample will also be assigned an identifying number by CLP FORMS II Lite software. Before or during the sampling event, the user will enter information regarding the site, project, sampling team, analysis, location, matrix (SB – soil boring, SW – surface water, MW – monitoring well), collection time and date, and sample and tag numbers.

When the laboratory receives a sample shipment, its LIMS will generate the in-house identification numbers in accordance with its sample receipt and chain-of-custody standard operating procedures (SOP).

QAPP WORKSHEET #28
QC SAMPLES TABLE

(UFP QAPP Section 3.4)
Complete a separate worksheet for each sampling technique, analytical method/SOP, matrix, analytical group, and concentration level. If method/SOP QC acceptance limits exceed the measurement performance criteria, the data obtained may be unusable for making project decisions.

Matrix	Soil
Analytical Group	CLP VOCs
Concentration Level	Low concentration
Sampling SOP	S-1, S-2, S-3
Analytical Method/ SOP Reference	A-1
Sampler's Name/ Organization	TBD/SulTRAC
Analytical Organization	CLP Laboratory
No. of Sampling Locations	See Worksheet #18

QC Sample	Frequency/ Number	Corrective Action (CA)	Person(s) Responsible for CA	DQI	Measurement Performance Criteria
Method Blank	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. If sufficient volume is not available, reanalyze affected extracts.	Laboratory Analyst	Accuracy/Bias Contamination	No target compounds > QL
MS/MSD	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. If sufficient volume is not available, reanalyze affected extracts.	Laboratory Analyst	Accuracy and Precision	%R and RPD as presented in Worksheet #12
Deuterated Monitoring Compounds	All samples	Reanalyze sample. If upon reanalysis, the monitoring compound meets criteria, report reanalysis results. If upon reanalysis, the monitoring compound does not meet criteria, the results are reported in the narrative.	Laboratory Analyst	Accuracy	%R as presented in Worksheet #12

QAPP WORKSHEET #28 (CONTINUED)
QC SAMPLES TABLE

Matrix	Soil
Analytical Group	CLP SVOCs
Concentration Level	Low concentration
Sampling SOP	S-1, S-2, S-3
Analytical Method/ SOP Reference	A-1
Sampler's Name/ Organization	TBD/SulTRAC
Analytical Organization	CLP Laboratory
No. of Sampling Locations	See Worksheet #18

QC Sample	Frequency/ Number	Corrective Action (CA)	Person(s) Responsible for CA	DQI	Measurement Performance Criteria
Method Blank	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. If sufficient volume is not available, reanalyze affected extracts.	Laboratory Analyst	Accuracy/Bias-Contamination	No target compounds > QL
MS/MSD	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. Otherwise, analyze laboratory control sample to see if problem is analysis or sample.	Laboratory Analyst	Accuracy and Precision	%R and RPD as presented in Worksheet #12
Deuterated monitoring compounds	All samples	Reanalyze sample. If upon reanalysis, the monitoring compound meets criteria, report reanalysis results. If upon reanalysis, the monitoring compound does not meet criteria, results are reported in narrative.	Laboratory Analyst	Accuracy	%R as presented in Worksheet #12

QAPP WORKSHEET #28 (CONTINUED)
QC SAMPLES TABLE

Matrix	Soil/Solids
Analytical Group	CLP PCBs
Concentration Level	NA
Sampling SOP	S-1, S-2, S-3
Analytical Method/ SOP Reference	A-1
Sampler's Name/ Organization	TBD/SulTRAC
Analytical Organization	CLP Laboratory
No. of Sampling Locations	See Worksheet #18

QC Sample	Frequency/ Number	Corrective Action (CA)	Person(s) Responsible for CA	DQI	Measurement Performance Criteria
Method Blank	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. If sufficient volume is not available, reanalyze affected extracts.	Laboratory Analyst	Accuracy/Bias-Contamination	No target compounds > QL
MS/MSD	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. Otherwise, analyze laboratory control sample to see if problem is analysis or sample.	Laboratory Analyst	Accuracy and Precision	%R and RPD as presented in Worksheet #12
Surrogate Spike	All samples	Reanalyze sample. If upon reanalysis, the surrogate meets criteria, report reanalysis results. If upon reanalysis, the surrogate does not meet criteria, the results are reported in the narrative.	Laboratory Analyst	Accuracy	30-150 %R

QAPP WORKSHEET #28 (CONTINUED)
QC SAMPLES TABLE

Matrix	Soil/Solids
Analytical Group	Metals and Cyanide
Concentration Level	NA
Sampling SOP	S-1, S-2, S-3
Analytical Method/ SOP Reference	A-2
Sampler's Name/ Organization	TBD/SulTRAC
Analytical Organization	TriMatrix Laboratories, Inc.
No. of Sampling Locations	See Worksheet #18

QC Sample	Frequency/ Number	Corrective Action (CA)	Person(s) Responsible for CA	DQI	Measurement Performance Criteria
Method Blank	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. If sufficient volume is not available, reanalyze affected extracts.	Laboratory Analyst	Sensitivity/ Contamination	No target compounds > QL
MS	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. Otherwise, analyze laboratory control sample to see if problem is analysis or sample.	Laboratory Analyst	Accuracy/Bias	75-125 %R (70-130 %R for mercury)
Laboratory Duplicate	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. Otherwise, analyze laboratory control sample to see if problem is analysis or sample.	Laboratory Analyst	Precision	<20% RPD

QAPP WORKSHEET #28 (CONTINUED)
QC SAMPLES TABLE

Matrix	Water
Analytical Group	CLP VOCs
Concentration Level	Low concentration
Sampling SOP	S-4, S-5
Analytical Method/ SOP Reference	A-1
Sampler's Name/ Organization	TBD/SulTRAC
Analytical Organization	CLP Laboratory
No. of Sampling Locations	See Worksheet #18

QC Sample	Frequency/ Number	Corrective Action (CA)	Person(s) Responsible for CA	DQI	Measurement Performance Criteria
Method Blank	1 per extraction batch samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. If sufficient volume is not available, reanalyze affected extracts.	Laboratory Analyst	Accuracy/Bias Contamination	No target compounds > QL
MS/MSD	1 per extraction batch samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. If sufficient volume is not available, reanalyze affected extracts.	Laboratory Analyst	Accuracy and Precision	%R and RPD as presented in Worksheet #12
Deuterated Monitoring Compounds	All samples	Reanalyze sample. If upon reanalysis, the monitoring compound meets criteria, report reanalysis results. If upon reanalysis, the monitoring compound does not meet criteria, the results are reported in the narrative.	Laboratory Analyst	Accuracy	%R as presented in Worksheet 12

QAPP WORKSHEET #28 (CONTINUED)
QC SAMPLES TABLE

Matrix	Water
Analytical Group	CLP SVOCs
Concentration Level	Low concentration
Sampling SOP	S-4, S-5
Analytical Method/ SOP Reference	A-1
Sampler's Name/ Organization	Robert Kondreck/SulTRAC
Analytical Organization	CLP Laboratory
No. of Sampling Locations	See Worksheet #18

QC Sample	Frequency/ Number	Corrective Action (CA)	Person(s) Responsible for CA	DQI	Measurement Performance Criteria
Method Blank	1 per extraction batch samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. If sufficient volume is not available, reanalyze affected extracts.	Laboratory Analyst	Accuracy/Bias-Contamination	No target compounds > QL
MS/MSD	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. Otherwise, analyze laboratory control sample to see if problem is analysis or sample.	Laboratory Analyst	Accuracy and Precision	%R and RPD as presented in Worksheet #12
Deuterated monitoring compounds	All samples	Reanalyze sample. If upon reanalysis, the monitoring compounds meets criteria, report reanalysis results. If upon reanalysis, the monitoring compound does not meet criteria, the results are reported in the narrative.	Laboratory Analyst	Accuracy	%R as presented in Worksheet #12

QAPP WORKSHEET #28 (CONTINUED)
QC SAMPLES TABLE

Matrix	Water
Analytical Group	CLP PCBs
Concentration Level	NA
Sampling SOP	S-4, S-5
Analytical Method/ SOP Reference	A-1
Sampler's Name/ Organization	TBD/SulTRAC
Analytical Organization	CLP Laboratory
No. of Sampling Locations	See Worksheet #18

QC Sample	Frequency/ Number	Corrective Action (CA)	Person(s) Responsible for CA	DQI	Measurement Performance Criteria
Method Blank	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. If sufficient volume is not available, reanalyze affected extracts.	Laboratory Analyst	Accuracy/Bias-Contamination	No target compounds > QL
MS/MSD	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. Otherwise, analyze laboratory control sample to see if problem is analysis or sample.	Laboratory Analyst	Accuracy and Precision	%R and RPD as presented in Worksheet #12
Surrogate Spike	All samples	Reanalyze sample. If upon reanalysis, the surrogate meets criteria, report reanalysis results. If upon reanalysis, the surrogate does not meet criteria, the results are reported in the narrative.	Laboratory Analyst	Accuracy	30-150 %R

QAPP WORKSHEET #28 (CONTINUED)
QC SAMPLES TABLE

Matrix	Water
Analytical Group	Metals and Cyanide
Concentration Level	NA
Sampling SOP	S-4, S-5
Analytical Method/ SOP Reference	A-2
Sampler's Name/ Organization	TBD/SulTRAC
Analytical Organization	TriMatrix Laboratories, Inc.
No. of Sampling Locations	See Worksheet #18

QC Sample	Frequency/ Number	Corrective Action (CA)	Person(s) Responsible for CA	DQI	Measurement Performance Criteria
Method Blank	1 per extraction batch samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. If sufficient volume is not available, reanalyze affected extracts.	Laboratory Analyst	Accuracy/Bias-Contamination	No target compounds > QL
MS	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch.	Laboratory Analyst	Accuracy/Bias	75-125 %R (70-130 %R for mercury)
Laboratory duplicate	1 per extraction batch of 20 samples maximum	If sufficient volume is available, extract and reanalyze samples in affected batch. Otherwise, analyze laboratory control sample to see if problem is analysis or sample.	Laboratory Analyst	Precision	<20% RPD (<24% for Method 1631)

Notes:

%R Percent recovery
CLP Contract Laboratory Program
DQI Data quality indicator
MS Matrix Spike
MS/MSD Matrix spike/matrix spike duplicate
NA Not applicable
PCB Polychlorinated biphenyl
QC Quality control
RPD Relative percent difference
TBD To be determined
VOC Volatile organic compound

QAPP WORKSHEET #29
PROJECT DOCUMENTS AND RECORDS TABLE

(UFP QAPP Section 3.5.1)
Identify the documents and records that will be generated for all aspects of the project including, but not limited to, sample collection and field measurement, on-site and off-site analysis, and data assessment. Identify where each document will be maintained.

Document	**Where Maintained**
Field notes/logbook	Project file (field data), SulTRAC offices
Chain of custody forms	Project file (laboratory data), SulTRAC offices
Laboratory raw data package (including electronic data deliverables)	EPA for CLP laboratory data; TriMatrix Laboratories, Inc., for its data; project file (laboratory data) at SulTRAC offices
Laboratory equipment calibration logs	EPA for CLP laboratory; TriMatrix Laboratories, Inc., for its data.
Validated data	Project file (laboratory data), SulTRAC offices

QAPP WORKSHEET #30
ANALYTICAL SERVICES TABLE

(UFP QAPP Section 3.5.2.3)
Identify all laboratories or organizations that will provide analytical services for the project, including on-site screening, on-site definitive, and off-site laboratory analytical work. Group by matrix, analytical group, concentration, and sample location or ID number. If applicable, identify the subcontractor laboratories and backup laboratory or organization that will be used if the primary laboratory or organization cannot be used.

Matrix	Analytical Group	Concentration Level	Sampling Location/ID Number	Analytical SOP[1]	Data Package Turnaround Time	Laboratory/Organization (Name and Address, Contact Person, and Telephone Number)	Backup Laboratory/Organization (Name and Address, Contact Person and Telephone Number)
Soil	VOCs SVOCs PCBs	Low concentration Low concentration NA	NA	A-1 A-1 A-1	21 days	CLP laboratory identified by EPA Region 5	CLP laboratory identified by EPA Region 5
Soil	Metals and cyanide	NA	NA	A-2	30 days	TriMatrix Laboratories, Inc. Grand Rapids, MI Phil Komar, (616) 846-9528	TestAmerica Laboratories, Inc. North Canton, Ohio Diane Jazdzyk (734) 205-2535
Water	VOCs SVOCs PCBs	Low concentration Low concentration NA	NA	A-1 A-1 A-1	21 days	CLP Laboratory identified by EPA Region 5	CLP Laboratory identified by EPA Region 5
Water[2]	Metals and cyanide	NA	NA	A-2	30 days	TriMatrix Laboratories, Inc. Grand Rapids, MI Phil Komar, (616) 846-9528	TestAmerica Laboratories, Inc. North Canton, Ohio Diane Jazdzyk (734) 205-2535

Notes:

1 See Worksheet #23 for identification of analytical methods.
2 Includes synthetic precipitation leaching procedure extract prepared from soil samples.
CLP Contract laboratory program
EPA U.S. Environmental Protection Agency
ID Identification
NA Not applicable
PCB Polychlorinated biphenyl
SOP Standard operating procedures
SVOC Semivolatile organic compound
VOC Volatile organic compound

QAPP WORKSHEET #31
PLANNED PROJECT ASSESSMENTS TABLE

(UFP QAPP Section 4.1.1)
Identify the type, frequency, and responsible parties of planned assessment activities that will be performed for the project.

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organization)	Person(s) Responsible for Responding to Assessment Findings (Title and Organization)	Person(s) Responsible for Identifying and Implementing CAs (Title and Organization)	Person(s) Responsible for Monitoring Effectiveness of CAs (Title and Organization)
No assessments planned	NA	NA	NA	NA	NA	NA	NA

Note:

NA Not applicable

QAPP WORKSHEET #32
ASSESSMENT FINDINGS AND CORRECTIVE ACTION RESPONSES

(UFP QAPP Section 4.1.2)
For each type of assessment, describe procedures for handling QAPP and project deviations encountered during the planned project assessments.

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Timeframe of Notification	Nature of CA Response Documentation	Individual(s) Receiving CA Response (Name, Title, Organization)	Timeframe for Response
No assessments planned	NA	NA	NA	NA	NA	NA

Note:

NA Not applicable

QAPP WORKSHEET #33
QA MANAGEMENT REPORTS TABLE

(UFP QAPP Section 4.2)
Identify the frequency and type of planned QA Management Reports, the project delivery dates, the personnel responsible for report preparation, and the report recipients.

Type of Report	Frequency (daily, weekly, monthly, quarterly, annually, etc.)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (Name, Title, Organization)	Report Recipient(s) (Title and Organization)
Data Validation Letter Report	To be determined	21 days after receipt of laboratory data packages	Jeffrey Lifka, Project Manager, SulTRAC	Sam Chummar, WAM, EPA Region 5
Data Evaluation Summary Report	At the end of the project	45 days after CLP- and TriMatrix validated data and PRP data	Jeffrey Lifka, Project Manager, SulTRAC	Sam Chummar, WAM, EPA Region 5

QAPP WORKSHEET #34
VERIFICATION (STEP I) PROCESS TABLE

(UFP QAPP Section 5.2.1)
Describe the processes that will be followed to verify project data. Describe how each item will be verified, when the activity will occur, and what documentation is necessary, and identify the person responsible. *Internal* or *external* is in relation to the data generator.

Verification Input	**Description**	**Internal/ External**	**Responsible for Verification (Name, Organization)**
Chain-of-custody forms	Chain-of-custody forms will be reviewed internally upon their completion and verified against the packed sample coolers they represent. The shipper's signature on the chain-of-custody form should be initialed by the reviewer, a copy of the chain-of-custody form should be retained in the project file, and the original and remaining copies should be taped inside the cooler for shipment.	Internal	TBD, SulTRAC
Field notes/ logbook	Field notes will be reviewed internally and placed in the project file. A copy of the field notes will be attached to each of the weekly oversight reports as generated as well as to the final report.	Internal	Jeffrey Lifka, SulTRAC
Laboratory data	All laboratory data packages will be verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal. All received data packages will be verified externally in accordance with the data validation procedures specified in Worksheet #35.	Internal External	CLP Laboratory and TriMatrix Laboratories, Inc. William Earle, SulTRAC

QAPP WORKSHEET #35
VALIDATION (STEPS IIA AND IIB) PROCESS TABLE

(UFP QAPP Section 5.2.2)
Describe the processes that will be followed to validate project data. Validation inputs include items such as those listed in Table 9 of the UFP-QAPP Manual (Section 5.1). Describe how each item will be validated, when the activity will occur, and what documentation is necessary and identify the person responsible. Differentiate between steps IIa and IIb of validation.

Step IIa/IIb	Validation Input	Description	Responsible for Validation (Name, Organization)[1]
IIa	Chain of custody	Examine traceability of samples from sample collection to sample analysis	EPA (CADRE), Analytical Coordinator, SulTRAC
IIa	Holding time	Confirm that holding time requirements are met	EPA (CADRE), Analytical Coordinator, SulTRAC
IIa	Instrument calibration	Confirm that instrument calibration requirements are met	EPA (CADRE), Analytical Coordinator, SulTRAC
IIa	Analytical method	Confirm that analytical methods are specified in QAPP	EPA (CADRE), Analytical Coordinator, SulTRAC
IIb	Performance criteria	Confirm that QC samples meet specified performance criteria; document any deviations in data evaluation summary report	EPA (CADRE), Analytical Coordinator, SulTRAC

Note:

1 U.S. Environmental Protection Agency (EPA) is responsible for conducting computer-aided data review and evaluation (CADRE) of analytical data generated by CLP laboratories. EPA review will be conducted in accordance with Contract Laboratory Program (CLP) National Functional Guidelines (NFG) for data validation. EPA will provide SulTRAC with a summary data review report.

QAPP WORKSHEET #36
VALIDATION (STEPS IIA AND IIB) SUMMARY TABLE

(UFP QAPP Section 5.2.2)
Identify the matrices, analytical groups, and concentration levels that each entity performing validation will be responsible for, as well as criteria that will be used to validate those data.

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (Title and Organization)
IIa	Soil/Solids	VOCs	Low	CADRE criteria and NFG	CADRE validation (EPA) and review of case narrative by SulTRAC
IIa	Soil/Solids	SVOCs	Low	CADRE criteria and NFG	CADRE validation (EPA) and review of case narrative by SulTRAC
IIa	Soil/Solids	PCBs	NA	CADRE criteria and NFG	CADRE validation (EPA) and review of case narrative by SulTRAC
IIa	Soil/Solids	Metals and Cyanide	NA	NFG and QAPP requirements	Validation by Analytical Coordinator, SulTRAC, or designated SulTRAC personnel
IIa	Water	VOCs	Low	CADRE criteria and NFG	CADRE validation (EPA) and review of case narrative by SulTRAC
IIa	Water	SVOCs	Low	CADRE criteria and NFG	CADRE validation (EPA) and review of case narrative by SulTRAC
IIa	Water	PCBs	NA	CADRE criteria and NFG	CADRE validation (EPA) and review of case narrative by SulTRAC
IIa	Water	Metals and Cyanide	NA	NFG and QAPP requirements	Validation by Analytical Coordinator, SulTRAC, or designated SulTRAC personnel

Notes:
[1] U.S. Environmental Protection Agency (EPA) is responsible for conducting CADRE of analytical data generated by the CLP laboratories. EPA review will be conducted in accordance with CLP NFG for data validation. EPA will provide SulTRAC with a summary data review report. The SulTRAC analytical coordinator will review this report to verify that project-specific QC criteria have been met. For the non-CLP analyses, SulTRAC will perform the entire data validation in accordance with CLP NFG as modified by project-specific requirements in this QAPP.

CADRE Computer-aided data review and evaluation
CLP Contract Laboratory Program
NA Not applicable
NFG National Functional Guidelines
PCB Polychlorinated biphenyl
QC Quality Control
SVOC Semi-volatile organic compound
VOC Volatile organic compounds

QAPP WORKSHEET #37
USABILITY ASSESSMENT

(UFP QAPP Section 5.2.3)
Describe the procedures/methods/activities that will be used to determine whether data are of the right type, quality, and quantity to support environmental decision-making for the project. Describe how data quality issues will be addressed and how limitations on the use of the data will be handled.

Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used: Usability of PRP data will be assessed by a comparison of analytical results provided by the PRP and by the CLP and subcontractor laboratory for split samples. Relative percent differences (RPD) between the PRP and CLP and subcontractor laboratory results will be calculated for each analyte detected.
Describe the evaluative procedures used to assess overall measurement error associated with the project: project: Overall measurement error will not be quantitatively assessed for this project. PRP data will be judged useable or not useable based on qualitative evaluation of RPD criteria. RPDs within 50% will be considered acceptable. At very low concentrations (near the analytical method detection limits), the data validator will use professional judgment, which may lead to acceptance of higher RPD.
Identify the personnel responsible for performing the usability assessment: SulTRAC's analytical coordinator will review analytical data and prepare the data validation report that will assess usability of the data. SulTRAC's project manager will review RPDs for split samples and assess overall usability of the data set in close consultation with the EPA WAM.
Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations), and anomalies: The usability assessment will be documented in a data evaluation summary report to be generated for each split sampling event. Any trends in usability of data will be determined by SulTRAC, which will report any trends relationships or anomalies to the EPA WAM. If PRP data consistently falls outside the RPD criterion, the EPA WAM may require modification of the PRP's analytical procedures.

APPENDIX A

TRIMATRIX LABORATORIES, INC.

STANDARD OPERATING PROCEDURES

- GR-18-106_REV 3.2(11-25-09)_CYANIDE MACRO-DISTILLATION_9010C 9013A
- GR-18-109_REV 3.4(11-25-09)_CYANIDE MIDI-DISTILLATION_9010C SM 4500 CN- B SM 4500 CN- C
- GR-05-122_REV 0.4(09-25-09)_CYANIDE KONELAB_4500-CN G 4500-CN E 9014
- GR-01-148_REV 0.3(01-20-09)_BLOCK DIGEST ICP-MS_3020A
- GR-01-147_REV 0.4(01-20-09)_BLOCK DIGEST for ICP_200.7 3010A
- GR-01-139_REV 0.2(08-15-09)_MERCURY BLOCK DIGEST SOIL_7471A
- GR-01-138_REV 0.6(01-20-09)_MERCURY_1631E
- GR-01-137_REV 1.5(02-01-09)_BLOCK DIG SOLIDS ICP ICPMS_3050B
- GR-01-129_REV 3.8(02-01-09)_ICPMS_6020A
- GR-01-123_REV 5.6(02-01-09)_MERCURY_245.1 7470A 7471A
- GR-01-117_REV 2.7(01-20-09)_SPLP_1312
- GR-01-100_REV 5.7(02-05-09)_ICP METALS_6010C
- GR-10-104_REV 2 2(04-06-09)_CoC

TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

Total and Amenable Cyanide Extraction and/or Macro-Distillation

SW-846 Method 9010C
SW-846 Method 9013A

APPROVALS:

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Operations Manager: Date: 11/13/09
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By: Tom C. Boocher

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Date Reviewed	Reviewed by	Review Expires

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1.0 SCOPE AND APPLICATION

1.1 This procedure is for the extraction and/or macro-distillation of soluble cyanide salts and many insoluble cyanide complexes. An extraction for oily, solid and multiphasic samples containing so much solid or solids of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask prior to the distillation is included.

1.2 The applicable concentration range is 0.05 to 10 mg/kg cyanide (dry weight).

1.3 The nominal reporting limit for soil and sludge samples is 0.05 mg/kg but varies based on percent solids. Waste samples are reported on an "as received" basis.

2.0 PRINCIPAL METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update IIIB, Revision 3, November, 2004, Method 9010C, "Total and Amenable Cyanide Distillation"

2.2 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* other methods, Revision 1, November, 2004, Method 9013A, "Cyanide Extraction Procedure for Solids and Oils"

3.0 SUMMARY OF PROCEDURE

3.1 If a sample contains so much solid or solids of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask or so much oil or grease as to interfere with the formation of a homogeneous emulsion, the sample is extracted with water at pH 10 or greater and the extract distilled and analyzed in accordance with TriMatrix SOP GR-05-122.

3.2 Samples of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask or have so much oil or grease as to interfere with the formation of a homogeneous emulsion and that contain free water are filtered and separated into an aqueous component and a combined oil/solid component. The oil/solid component is extracted and an aliquot of the aqueous extract is combined with an aliquot of the filtrate in proportion to the sample composition. Alternatively, sample components may be analyzed separately and cyanide reported for each component.

3.3 If sample solids are known to contain sufficient levels of cyanide (≥50 mg/kg) as to be well above the method detection limit (MDL), the extraction step may be deleted and the solids distilled directly by diluting a small aliquot of the high-concentration solid (1-10 g) in 500 mL of water in the distillation flask and suspending the slurry during distillation.

3.4 Distillation of the sample or sample extract then releases cyanide as hydrogen cyanide gas (HCN) by the addition of sulfuric acid which is collected in a sodium hydroxide (NaOH) scrubber trap.

3.5 The NaOH trap solution is then analyzed in accordance with TriMatrix SOP GR-05-122.

4.0 PARAMETER OR COMPOUND LIST

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4.1 Total or Extractable Cyanide

4.2 Total or Extractable Amenable Cyanide

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-05-122, *Total Cyanide by Konelab UV Spectrophotometry*, latest revision

5.2 TriMatrix SOP GR-15-100, *Laboratory Waste Disposal*, latest revision

5.3 TriMatrix SOP GR-10-106, *Inorganic and Metals Laboratories Corrective Actions*, latest revision

5.4 TriMatrix SOP GR-09-128, *Homogenization, Grinding and Drying of Solid Samples*, latest revision

5.5 TriMatrix SOP GR-10-125, *Method Detection Limit (MDL)*, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Most interfering substances are removed by the distillation.

6.2 Sulfides adversely affect the colorimetric analysis. Sulfides are removed by the addition of bismuth nitrate prior to distillation.

6.3 Results are biased high for samples containing nitrate and/or nitrite without pre-treatment. During distillation, nitrate and nitrite forms nitrous acid which reacts with some organic compounds to form oximes. These compounds decompose to generate HCN. Nitrate and nitrite interference is eliminated by pre-treatment with sulfamic acid.

6.4 Oxidizing agents can cause negative interference by destroying cyanide-containing compounds. This interference is removed by treating with ascorbic acid.

7.0 SAFETY PRECAUTIONS

7.1 Comply with all instructions for health and safety as outlined in the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan.

7.2 Heating mantles are hot during use. Avoid contact to prevent burns.

7.3 This procedure involves acidifying samples that potentially contain high levels of cyanide. The acidification and distillation must be carried out under a fume hood.

7.4 Avoid contact with laboratory chemicals and solutions. Especially avoid contact with sulfuric acid and sodium hydroxide.

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7.5 Approved safety glasses, disposable gloves and a laboratory coat are mandatory when working in the wet chemistry laboratory.

7.6 Potassium cyanide (KCN) is a violent poison. Avoid any type of contact. Do not breathe KCN dust or vapor. Always open the container and perform all dilutions in a fume hood. Keep potassium cyanide away from acids. If necessary, use a particle face mask when working with the chemical to further minimize exposure.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Waste, sludge and soil samples are to be collected in inert bottles with no preservative added.

8.2 Store all samples at 0 - 6° C until analysis.

8.3 Homogenize waste, sludge and soil samples thoroughly inside a laboratory hood, in accordance with TriMatrix GR-09-128, prior to sub-sampling for extraction and/or distillation.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Distillation apparatus is shown in Attachment 20.1 and contains parts as follows:

9.1.1 Distilling flask, 1 L in volume

9.1.2 Inlet tube

9.1.3 Condenser with cooling water

9.1.4 Hydrogen cyanide (HCN) scrubber trap

9.1.5 Low-vacuum source

9.2 Volumetric flasks, various sizes, type A

9.3 Volumetric pipets, various sizes, type A

9.4 Autopipetter, confirmed traceable to NIST standards at each volume measured

9.4 Balance, top-loading, readable to 0.01 g

9.5 Graduated cylinders, various sizes

9.6 TCLP Tumbler – This device sufficiently agitates a 1 L sealed glass container. For the purpose of this analysis, agitation is sufficient when:

9.6.1 All sample surfaces are continuously brought into contact with the extraction fluid.

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9.6.2 The agitation prevents stratification of the sample and extraction fluid.

9.7 Buchner funnel apparatus:

9.7.1 Buchner funnel, 500 mL capacity with 1-liter vacuum filtration flask.

9.7.2 Filters, 0.45 µm, glass fiber

9.7.3 Vacuum source

9.8 Separatory funnels, glass, 500 mL or larger

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 After each batch, wipe all distillation heating mantles and counter areas clean.

10.2 Carefully inspect each part of the distillation glassware before use. Cracked or chipped glassware must be repaired and/or replaced. Do not use cracked or chipped glassware.

11.0 CHEMICALS AND REAGENTS

11.1 Laboratory Reagent Water, ASTM Type II, Milli-Q water system

11.2 Sodium Hydroxide (NaOH), ACS grade pellets or better

11.3 Bismuth Nitrate pentahydrate ($Bi(NO_3)\cdot 5H_2O$), certified reagent grade powder or better

11.4 Concentrated Sulfuric Acid (H_2SO_4), technical grade or better

11.5 Potassium Cyanide (KCN), ACS grade crystals or better

11.6 Magnesium Chloride, hexahydrate ($MgCl_2\cdot 6H_2O$), ACS grade crystals or better

11.7 Sulfamic Acid (NH_2SO_3H), certified reagent grade crystalline powder or better

11.8 Potassium iodide/starch test paper

11.9 Prepare sodium hydroxide solution (1.25N) as follows:

11.9.1 Dissolve 50.0 g of sodium hydroxide pellets into a 1000 mL volumetric flask partially filled with laboratory reagent water.

11.9.2 Dilute to volume with laboratory reagent water after the solution cools.

11.9.3 Expiration is six months from the date made if stored tightly capped in an inert plastic or glass container.

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11.10 Prepare bismuth nitrate solution as follows:

11.10.1 Dissolve 30.0 g of $Bi(NO_3)_3 \cdot 5H_2O$ into a 1000 mL volumetric flask filled with approximately 100 mL reagent water. Stir until dissolved.

11.10.2 While stirring, add 250 mL of glacial acetic acid.

11.10.3 Dilute to volume with laboratory reagent water.

11.10.4 Expiration is six months from the date made if stored tightly capped in an inert plastic or glass container.

11.11 Prepare magnesium chloride solution as follows:

11.11.1 Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 mL volumetric flask partially filled with laboratory reagent water.

11.11.2 Stir to dissolve, dilute to volume with reagent water.

11.11.3 Expiration is six months from the date made if stored tightly capped in an inert plastic or glass container.

11.12 Prepare sulfamic acid solution as follows:

11.12.1 Dissolve 40 g of NH_2SO_3H in a 1000 mL volumetric flask partially filled with laboratory reagent water.

11.12.2 Dilute to volume with reagent water.

11.12.3 Expiration is six months from the date made if stored tightly capped in an inert plastic or glass container.

11.13 Glacial Acetic Acid ($C_2H_4O_2$), ACS grade or better

11.14 Anhydrous Sodium Acetate ($C_2H_3O_2Na$): ACS grade

11.15 Prepare acetate buffer solution (pH = 4.0) as follows:

11.15.1 Dissolve 7.3 g anhydrous sodium acetate in a 50 mL volumetric flask filled with approximately 20 mL laboratory reagent water.

11.15.2 Add 24 g glacial acetic acid then dilute to volume with laboratory reagent water.

11.15.3 Expiration is six months from the date made if stored tightly capped in an inert plastic or glass container.

11.16 Lead Acetate Paper

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11.17 Sodium hydroxide solution (50%, w/v), prepare as follows (in a fume hood):

11.17.1 Weigh out 150 g of sodium hydroxide (NaOH) pellets on a top-loading balance in a 1000 mL beaker.

11.17.2 Slowly add laboratory reagent water to the beaker until the pellets dissolve then add laboratory reagent water to the 300 mL mark on the beaker. Be careful not to add water so fast that splashing occurs from the heat of dissolution.

11.17.3 After cooling (on the bench and in the hood), transfer to a glass container and store at room temperature tightly capped.

11.17.4 Expiration is 6 months from the date prepared.

11.18 Hexane, pesticides grade or better

12.0 STANDARDS PREPARATION

12.1 Any sample treated with bismuth nitrate for sulfide interference (Section 13.5) must be quantitated using a calibration curve run with standards that have also been treated with bismuth nitrate.

12.2 Standards preparation is described in TriMatrix SOP GR-05-122, Section 12.0.

13.0 ANALYTICAL PROCEDURE

13.1 If a sample contains so much solid or solids of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask or contains so much oil or grease as to interfere with the formation of a homogeneous emulsion, and does not contain any free aqueous phase, extract as follows:

13.1.1 Place the following in a 1 L wide-mouthed glass bottle:

13.1.1.1 500 mL laboratory reagent water

13.1.1.2 5 mL of 50% w/v sodium hydroxide (NaOH) solution

13.1.1.3 50 mL n-Hexane (only if a heavy grease is present)

13.1.1.4 A representative sample aliquot of 25 g (based on dry weight), determined as follows:

$$\text{grams needed} = \frac{0.005 \text{ mg/L} \times 250 \text{ mL} \times 100}{A \times B}$$

Where:

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A = Reporting limit, in mg/kg (dry weight)
B = Sample percent solids

13.1.2 Cap the bottle.

13.1.3 The extract pH must be maintained above 10 throughout the extraction and subsequent filtration. Since some samples may release acid, monitor the pH as follows:

13.1.3.1 Shake the extraction bottle and after one minute, check the pH.

13.1.3.2 If the pH is below 12, add 50% NaOH in 5 mL increments until it is at least 12.

13.1.3.3 Recap the bottle and repeat until the pH does not drop below 12.

13.1.4 Place the capped bottle in the TCLP tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 16 - 18 hours.

13.1.5 Prepare a Buchner funnel with a glass fiber filter and decant the extract to the Buchner funnel. Full recovery of the extract is not necessary. However, filter at least 250 mL unless the cyanide concentration is expected to be high.

13.1.6 If the extract contains an oil phase and/or hexane was added before extracting, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical but are necessary to be able to measure the aliquot volume of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere with the distillation or analysis.

13.1.7 Proceed to Section 13.5 for the distillation step.

13.2 If the sample is a homogeneous fluid or slurry that does not separate or settle in the distillation flask when mixing so the solids are entirely suspended then distill as a water without the solids extraction step by using 250 mL of sample and 250 mL of laboratory reagent water to distill a 500 mL total volume. Refer to Section 13.5 for the distillation step.

13.3 If the sample is multi-phasic and contains so much solid or solids of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask or contains so much oil or grease as to interfere with the formation of a homogeneous emulsion, extract as follows:

13.3.1 Assemble a Buchner funnel apparatus. Insert a weighed glass fiber filter (weigh the pad then place it in the funnel). Turn the vacuum on and wet the pad with a known volume of water.

13.3.2 Transfer the sample to the Buchner funnel in small aliquots, first decanting the fluid. Rinse the sample container with known volumes of water and add the rinses to the Buchner funnel. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber filter but this will not interfere with the analysis.

13.3.3 Transfer the solid and glass fiber filter to a tared weighing dish. Since most greases and oils will not pass through the filter, solids, oils and greases can be extracted together. If the filtrate

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includes an oil phase, transfer the filtrate to a separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid.

13.3.4 Weigh the dish containing solid, oil (if any) and filter. Subtract the mass of the dry filter pad. Calculate the net volume of water present in the original sample by subtracting the total volume of rinses used from the measured volume of the filtrate.

13.3.5 Place the following in a 1 L wide-mouthed glass bottle:

13.3.5.1 500 mL laboratory reagent water

13.3.5.2 5 mL 50% w/v NaOH

13.3.5.3 50 mL n-Hexane (if a heavy waste-insoluble grease is present)

13.3.5.4 If the mass of the solids is greater than 25 g, weigh out a representative aliquot of 25 g and add it to the bottle; otherwise add all of the solids and the filter. Cap the bottle tightly.

13.3.6 Maintain the extract pH above 10 throughout the extraction and subsequent filtration. Since some samples may release acid, monitor the pH as follows:

13.3.6.1 Shake the extraction bottle and after one minute, check the pH.

13.3.6.2 If the pH is below 12, add 50% w/v NaOH in 5 mL increments until it is at least 12.

13.3.6.3 Recap the bottle and repeat until the pH does not drop below 12.

13.3.7 Place the bottle in the TCLP tumbler, making sure there is enough cushioning foam insulation. Turn the tumbler on and allow the extraction to run for 16 – 18 hours.

13.3.8 Assemble a Buchner funnel with a glass fiber filter.

13.3.9 Decant the extract to the Buchner funnel. Full recovery of the extract is not necessary.

13.3.10 If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor filtration are critical but are necessary to be able to measure the volume of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere.

13.3.11 At this point, an aliquot of the filtrate from the original sample may be combined with an aliquot of the solids extract in volumes proportional and representative of the sample, as the following equation illustrates. The distillation step is in Section 13.5. Alternatively, each may be distilled and analyzed separately and concentrations reported for each phase if specified.

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$$\frac{\text{Liquid Sample Aliquot (mL)}}{\text{Extract Aliquot(mL)}} = \frac{\text{Solid Sample Mass extracted (g)}}{\text{(Solids \& oil phase) - (dry weight filter + tared dish) (g)}} \times \frac{\text{Filtrate Volume including rinses (mL)}}{\text{500 mL extraction fluid + NaOH (mL)}}$$

13.4 Pretreatment for cyanides amenable to chlorination if distilling for amenable cyanides is as follows:

13.4.1 The amenable cyanide pretreatment must be performed under amber light since $K_3[Fe\text{-}(CN)_6]$ decomposes under UV light and hence will test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination. One treated and one untreated.

13.4.2 To 250 mL sample or solid/oil extract diluted to 500 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25M sodium hydroxide until an excess of chlorine is present as indicated by potassium iodide (KI) starch paper turning blue. The sample will be subjected to alkaline chlorination by this step.

Caution: The initial alkaline chlorination reaction product is cyanogen chloride. This reaction MUST be performed in a fume hood.

13.4.3 Test for excess chlorine with KI starch paper and maintain an excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution.

13.4.4 After one hour, add 0.2 g of L-ascorbic acid until KI-starch paper indicates no residual chlorine. Then add 0.2 g of L-ascorbic acid to ensure the presence of excess reducing agent. This is the chlorinated aliquot.

13.4.5 Distill then analyze for total cyanide in the chlorinated and the unchlorinated sample aliquots in accordance with TriMatrix SOP GR-05-122. The difference between the chlorinated and unchlorinated aliquots is equal to the cyanide amenable to chlorination concentration.

13.5 The distillation is as follows:

13.5.1 Place 250 mL of extract or up to 25 g sample diluted to 500 mL in the one liter distillation flask.

13.5.2 Pipet 50 mL of 1.25M sodium hydroxide into the gas scrubber. Connect the flask, condenser, gas scrubber and vacuum trap.

13.5.3 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the air inlet tube.

13.5.4 Use potassium iodide starch test paper dampened with acetate buffer to test for oxidizing agents. If the test paper turns blue, add 0.2 ±0.1 g ascorbic acid powder then stir and test again. Repeat until the paper no longer turns blue then add 0.05 ±0.1 g of additional ascorbic acid powder.

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13.5.5 If a sample is known or suspected to contain sulfide, add 50 mL of 0.062M bismuth nitrate solution through the air inlet tube. Mix for three minutes. Use lead acetate paper to check the sample for the presence of sulfides. A positive test is indicated by a black color on the paper.

Note: Associated quality control samples must also be treated when this step is used.

13.5.6 If a sample is known or suspected to contain nitrate or nitrite, or if bismuth nitrate was added to the sample, add 50 mL of 0.4N sulfamic acid solution through the air inlet tube. Mix for three minutes.

Note: Associated quality control samples must also be treated when this step is used.

13.5.7 Slowly add 25 mL of concentrated sulfuric acid through the air inlet tube. Rinse the tube with water and allow the airflow to mix the flask contents for three minutes.

13.5.8 Add 20 mL of 2.5M magnesium chloride through the air inlet and wash the inlet tube with a stream of water.

13.5.9 Heat the solution to boiling then reflux for one hour. Turn off the heat and continue the airflow for at least 15 minutes. After cooling the flask and closing the vacuum source, disconnect the gas scrubber.

13.5.10 Transfer the scrubber solution to a 250-mL volumetric flask, rinse the scrubber into the volumetric flask and dilute to volume with laboratory reagent water.

13.5.11 Proceed to the cyanide analysis in accordance with TriMatrix SOP GR-05-122.

Note: If distillates are not analyzed immediately, store tightly sealed away from light.

14.0 DATA REPORTING AND DELIVERABLES

14.1 Record all data in Element™ for each batch distilled, including the following.

14.1.1 Sample mass distilled, in g

14.1.2 Spiking solution concentrations, in mg/L

14.1.3 Spiking solution volume used, in mL

14.1.4 Analyst initials

14.1.5 Date of distillation

14.1.6 Batch number

14.2 Refer to Attachment 20.2 for an Element™ Preparation Batch Report example.

Approved By: pos 11-13-09 **QA Officer** **Approved By:** Heather L Brady **Area Supervisor**

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15.0 QUALITY ASSURANCE

15.1 Method and matrix QC must be distilled for each batch. A batch consists of a maximum of 20 samples per matrix and may be left open for up to 14 days.

15.1.1 Distillation QC consists of two Blank Spikes (BS), a Method Preparation Blank (BLK) each day samples are distilled and each time a new batch is opened, and a Matrix Spike/Matrix Spike Duplicate (MS/MSD) for each batch of up to 20 samples.

15.1.1.1 The BS is an aliquot of stock standard spiked into up to 25 g of Ottawa sand and 500 mL of laboratory reagent water, distilled and analyzed like a sample.

15.1.1.1.1 To prepare the low-concentration BS, measure 25 g of Ottawa sand and 500 mL of laboratory reagent water into a 1 L distillation flask. Pipet 125 µL of 100 mg/L cyanide standard directly into the bottle then distill as a sample. The BS concentration is 0.5 mg/kg cyanide based on a 25 g sample distillation.

$$\frac{100\text{ mg}}{\text{L}}\ \frac{0.125\text{ mL}}{25\text{ g}} = 0.5\text{ mg/kg CN}^-$$

15.1.1.1.2 To prepare the high concentration blank spike, measure 25 g Ottawa sand and 500 mL of laboratory reagent water into a 1 L distillation flask. Pipet 250 µL of 100 mg/L cyanide standard directly into the flask then distill as a sample. The BS concentration is 1.0 mg/kg cyanide based on a 25 g sample distillation.

$$\frac{100\text{ mg}}{\text{L}}\ \frac{0.250\text{ mL}}{25\text{ g}} = 1.0\text{ mg/kg CN}^-$$

15.1.1.1.3 To prepare matrix spikes, measure up to 25 g of sample (using approximately the same amount for the MSD) and 500 mL of laboratory reagent water into a 1 L distillation flask. Pipet 250 µL of 100 mg/L cyanide standard directly into the flask then distill as a sample. The MS and/or MSD spiked concentration is 1.0 mg/kg cyanide based on 25 g sample distillation.

$$\frac{100\text{ mg}}{\text{L}}\ \frac{0.250\text{ mL}}{25\text{ g}} = 1.0\text{ mg/kg CN}^-$$

15.1.1.2 The BLK is 25 g Ottawa sand and 500 mL of laboratory reagent water distilled as a sample. Calculate the result based on a 25 g sample.

Note: Place QC randomly in the distillation setup. Do not use the same position each time.

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15.1.2 Extraction QC consists of Blank Spike (BS), a Method Preparation Blank (BLK) each day samples are extracted and each time a new batch is opened, and a Matrix Spike/Matrix Spike Duplicate (MS/MSD) for each batch of up to 20 samples.

15.1.2.1 The BS is an aliquot of stock standard spiked into laboratory reagent water, extracted, filtered, distilled and analyzed like a sample.

15.1.2.1.1 To prepare the blank spike, measure 25 g of Ottawa sand and 500 mL of laboratory reagent water into a 1 L extraction bottle. Pipet 250 µL (or 50 µL for available cyanide) of 100 mg/L cyanide standard directly into the bottle then extract, filter and distill as a sample. The BS concentration is 1.0 mg/kg cyanide (or 0.2 mg/kg for available cyanide) based on a 25 g sample extraction and 250 mL extract distillation.

$$\frac{100\text{ mg}}{1\text{ L}} \Bigg| \frac{0.250\text{ mL}}{500\text{ mL}} = 0.05\text{ mg/L } CN^- \text{ at instrument}$$

$$\frac{0.05\text{ mg}}{1000\text{ mL}} \Bigg| \frac{250\text{ mL}}{250\text{ mL}} \Bigg| \frac{500\text{ mL}}{25\text{ g}} \Bigg| \frac{1000\text{ g}}{\text{kg}} = 1.0\text{ mg/kg } CN^- \text{ in sample}$$

15.1.2.2 The MS is an aliquot of stock standard spiked into no more than 25 g of sample and 500 mL of laboratory reagent water, extracted, and filtered, distilled and analyzed like a sample. The MSD is identical with approximately the same sample mass used.

15.1.2.2.1 To prepare the matrix spike, measure 25 g of sample and 500 mL of laboratory reagent water into a 1 L extraction bottle. Pipet 250 µL (or 50 µL for available cyanide) of 100 mg/L cyanide standard directly into the bottle then extract, filter and distill as a sample. The spiked concentration is 1.0 mg/kg cyanide (or 0.2 mg/kg for available cyanide) based on a 25 g sample extraction and 250 mL extract distillation.

$$\frac{100\text{ mg}}{1\text{ L}} \Bigg| \frac{0.250\text{ mL}}{500\text{ mL}} = 0.05\text{ mg/L } CN^- \text{ at instrument}$$

$$\frac{0.05\text{ mg}}{1000\text{ mL}} \Bigg| \frac{250\text{ mL}}{250\text{ mL}} \Bigg| \frac{500\text{ mL}}{25\text{ g}} \Bigg| \frac{1000\text{ g}}{\text{kg}} = 1.0\text{ mg/kg } CN^- \text{ in sample}$$

15.1.2.3 The BLK is 25 g of Ottawa sand and 500 mL of laboratory reagent water extracted, filtered and distilled as a sample. Calculate the result based on a 25 g sample extraction.

Note: If the sample being spiked has a high cyanide concentration, adjust the sample aliquot used to less than 25 g and/or spike at a higher concentration as necessary.

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15.2 Refer to TriMatrix SOP GR-10-106 for corrective action to be taken when quality control is unacceptable.

16.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

16.1 Before processing actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC). Each analyst responsible for sample processing by this procedure must pass an IDC.

16.1.1 Initial Demonstration of Capability (IDC) Study

16.1.1.1 Prepare four blank spikes (using a stock standard separate from the calibration stock) at 0.5 mg/kg. Extract, filter, distill and analyze the four spikes following every step in this and the analytical procedure.

16.1.1.2 Input the four results to the IDC spreadsheet located on the laboratory intranet library to calculate average percent recovery and relative standard deviation.

16.1.1.3 Average percent recovery must fall within blank spike acceptance limits.

16.1.1.4 Relative standard deviation must be ≤20%.

16.1.1.5 If either criterion is not met, locate and correct the source of the problem and repeat the study. Repeated failure however, will indicate a problem with the techniques and/or the procedure. If this occurs, locate the problem, correct the techniques and/or procedure then repeat the study successfully.

16.1.1.6 Samples may not be processed by the analyst until an IDC study has been successfully completed.

16.1.1.7 Give a copy of all attempted IDC spreadsheets and raw data to Quality Assurance for training and documentation.

16.1.2 Continuing Demonstration of Capability (CDC) Study

16.1.2.1 Annually a CDC is required by each analyst.

16.1.2.2 The CDC may be accomplished by any of the following approaches:

16.1.2.2.1 By repeating the IDC study

16.1.2.2.2 By using the last four results from the annual method detection limit study if run exclusively by the analyst. Use only the last four results.

16.1.2.2.3 By using four consecutive blank spikes from routine sample analysis if run exclusively by the analyst.

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16.1.2.2.4 By successfully and exclusively running a PT study performed during the course of routine sample analysis.

16.1.2.3 Process CDC data using the same spreadsheet used for the IDC study.

16.2 A Method Detection Limit (MDL) study must be performed annually for this procedure in accordance with TriMatrix SOP GR-10-125.

17.0 POLLUTION PREVENTION

17.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

17.2 Never dispose of laboratory chemicals without first referencing appropriate written instructions of disposal for that particular material.

17.3 Conserve the use of chemicals where applicable.

17.4 Comply with all environmental laws associated with chemicals in the laboratory.

18.0 WASTE MANAGEMENT

18.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals.

18.2 To minimize the environmental impact and costs associated with chemical disposal, order and use only the minimum amount of material required.

18.3 Follow all instructions in TriMatrix SOP GR-15-102 for laboratory waste disposal requirements.

19.0 REFERENCES

19.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update IIIB, Revision 3, November, 2004, Method 9010C, "Total and Amenable Cyanide Distillation"

19.2 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* other methods, Revision 1, November, 2004, Method 9013A, "Cyanide Extraction Procedure for Solids and Oils"

20.0 ATTACHMENTS

20.1 Example Diagram of Apparatus for Cyanide Distillation

20.2 Element™ Preparation Batch Report Example

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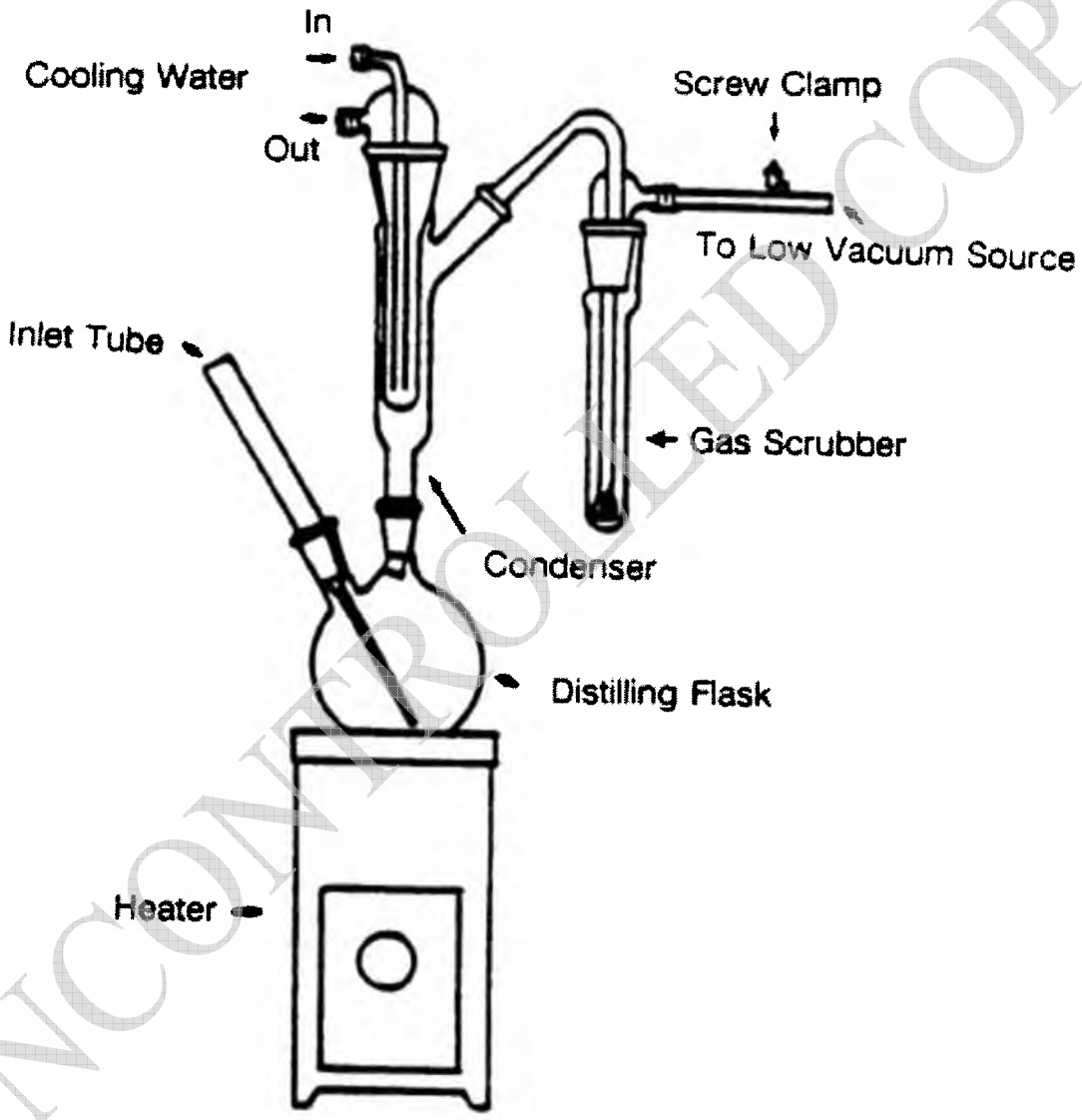
Attachment 20.1
Example Diagram of Apparatus for Cyanide Distillation



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Attachment 20.2
Element™ Preparation Batch Report Example

TriMatrix Laboratories, Inc.

PREPARATION BATCH 0903726 Page 1 of 1

Printed: 11/12/2009 12:04:00PM

Inorganic - Wet Chemistry, Soil, 9010B Cyanide Distillation

(No Surrogate)

Batch Comments: (none)

Work Order	Analysis	Work Order	Analysis	Work Order	Analysis
0904051	Cyanide, Amenable 9014				

Lab Number	Contain	Prepared	By	Initial (g)	Final (mL)	uL Surrogate	Source ID	Spike ID	uL Spike	Client / QC Type	Extraction Comments
0903726-BLK1		Apr-06-09 07:00	LMA	25.33	250					BLANK	
0903726-DUP1		Apr-06-09 07:00	LMA	24.89	250		0904051-01			DUPLICATE	
0903726-BS1		Apr-06-09 07:00	LMA	25.87	250			9040185	250	LCS	
0903726-BS2		Apr-06-09 07:00	LMA	25.15	250			9040185	125	LCS	
0904051-01	A	Apr-06-09 07:00	LMA	24.75	250					[redacted]	

Comments:	Analyst Initials

bch_TriMatrix.rpt

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Approved By: 11-13-09 **QA Officer**

Approved By: Heather L. Brady **Area Supervisor**

TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

Midi-Distillation for Cyanide

Standard Methods 4500-CN⁻ B, Standard Methods 4500-CN⁻ C
SW-846 Method 9010C

APPROVALS:

Area Supervisor: Heather L. Brady Date: 11-13-09
Heather L. Brady

QA Officer: Date: 11-12-09
Tom C. Boocher

Operations Manager: Date: 11/13/09
Jeff P. Glaser

Procedure Number: GR-18-109
Revision Number: 3.4

Date Initiated: 7/23/93
Effective Date: 11/25/09

Date Revised: 11/12/09
Pages Revised: All

By: Lucy M. Asbury

Total Number of Pages: 13

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

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1.0 SCOPE AND APPLICATION

1.1 This procedure is applicable to the midi-distillation of inorganic cyanides, present as simple soluble salts or complex radicals in water and wastewater.

1.2 The applicable concentration range is 0.005 mg/L to 0.2 mg/L.

1.3 The reporting limit is 0.005 mg/L.

2.0 PRINCIPAL METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update IV, Revision 3, November 2004, Method 9010C, "Total and Amenable Cyanide Distillation"

2.2 *Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1995,* 4500-CN⁻ B, Cyanide, Preliminary Treatment of Samples

2.3 *Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1995,* 4500-CN⁻ C, Cyanide, Total Cyanide after Distillation

3.0 SUMMARY OF PROCEDURE

3.1 Cyanide present in a sample is released as a gas (HCN) upon addition of sulfuric acid (H_2SO_4). The HCN is collected in a sodium hydroxide (NaOH) scrubber. The NaOH solution from the scrubber is analyzed for cyanide in accordance with TriMatrix SOP GR-02-100 or GR-05-122.

3.2 Due to safety and waste considerations, the procedure uses bismuth nitrate as specified in method 9010C to eliminate sulfide interferences rather than powdered cadmium or lead carbonate as specified in methods 335.4 and 4500-CN⁻ C.

3.3 The procedure uses a midi-distillation block rather than the macro-distillation glassware specified in method 4500-CN⁻ C.

4.0 PARAMETER OR COMPOUND LIST

4.1 Total Cyanide

5.0 REFERENCED SOPs

5.1 TriMatrix Laboratories SOP GR-02-100, *Cyanide, Total, Lachat Autoanalyzer*, latest revision

5.2 TriMatrix Laboratories SOP GR-05-122, *Total Cyanide by Konelab UV Spectrophotometry*, latest revision

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5.3 TriMatrix Laboratories SOP GR-15-102, *Laboratory Waste Disposal*, latest revision

5.4 Andrews Glass Company, *Midi-Distillation System*, Model 110-10, Instruction Manual

5.5 TriMatrix Laboratories SOP GR-10-106, *Inorganic and Metals Laboratories Corrective Actions*, latest revision

5.6 TriMatrix Laboratories SOP GR-10-125, *Method Detection Limit (MDL)*, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Most interfering substances are removed by the distillation. However, sulfides, oxidizing agents, nitrates and nitrites are not removed. Detection of sulfides and oxidizing agents in a sample will require preliminary cleanup. All samples are treated to remove nitrate and nitrite interference.

6.2 Sulfides adversely affect the colorimetric determination and must be removed by addition of bismuth nitrate solution prior to distillation. Refer to Section 13.2.

6.3 Oxidizing agents such as residual chlorine cause a negative interference by destroying cyanide-containing compounds and must be removed by treating with ascorbic acid. Refer to Section 13.3.

6.4 High results are obtained for samples containing nitrates and/or nitrites. During the distillation, nitrates and nitrites form nitrous acid that reacts with some organic compounds to form oximes. These oximes decompose to generate HCN. Nitrate/nitrite interference must be removed by pre-treatment with sulfamic acid. Refer to Section 13.19.

7.0 SAFETY PRECAUTIONS

7.1 Comply with all instructions for health and safety as outlined in the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan.

7.2 The heating block is hot during use. Precautions must be taken to avoid burns.

7.3 This procedure involves acidifying samples with potentially high cyanide levels. The distillation must be performed under an appropriate fume hood.

7.4 Avoid contact exposure with sulfuric acid and sodium hydroxide or any other chemical in the laboratory. Approved safety glasses, disposable gloves and a laboratory coat are required personal protective equipment (PPE) when working in the inorganic laboratory and while performing this procedure.

7.5 Potassium cyanide (KCN) is a violent poison. Precautions must be taken to avoid contact exposure, inhalation of dust or vapor and consequential ingestion. Always open containers and dilute all solutions in a fume hood wearing PPE. Keep potassium cyanide away from acids.

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8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Water and wastewater are collected in opaque brown, inert plastic bottles and preserved with sodium hydroxide to pH >12. Analysis must be performed within 14 days of sample collection.

8.2 All samples must be stored in the laboratory at 0 - 6° C until the time of analysis.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Reflux distillation apparatus as shown in Attachment 20.1

9.2 Midi-distillation block

9.3 Volumetric flasks, glass, various sizes, type A

9.4 Volumetric pipets, glass, various sizes, type A

9.5 Balance, top-loading, readable to 0.01 g

9.6 Balance, analytical, readable to 0.0001 g

9.7 Graduated cylinders, various sizes

9.8 Boiling chips, clean and inert

9.9 Lead acetate paper, to check for sulfides

9.10 Specimen Cups, plastic, for scrubber/absorber solution storage

9.11 Micropipettes

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Clean the midi-distillation heating block after each use by wiping with a clean damp paper towel or cloth.

10.2 All glassware must be inspected for chips or cracks before use. Chipped or cracked glassware must be repaired or replaced.

11.0 CHEMICALS AND REAGENTS

11.1 Laboratory Reagent Water, ASTM Type II, Milli-Q system

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11.2 Sodium Hydroxide (NaOH), ACS grade or better

11.3 Bismuth Nitrate, 5-Hydrate ($Bi(NO_3)\cdot 5H_2O$), certified grade or better

11.4 Concentrated Sulfuric Acid (H_2SO_4), technical grade or better

11.5 Sulfuric Acid Solution (1:1 v/v) – Slowly and carefully add 500 mL of concentrated H_2SO_4 to 500 mL of laboratory reagent water. Cool to room temperature before use. Store in glass. Expiration is 6 months from the date made.

11.6 Potassium Cyanide (KCN), ACS grade or better

11.7 Magnesium Chloride, hexa-hydrate ($MgCl_2\cdot 6H_2O$), ACS grade or better

11.8 Sulfamic Acid (NH_2SO_3H), certified

11.9 L-Ascorbic Acid ($C_6H_8O_6$), ACS grade or better

11.10 Potassium iodide-starch test paper, to check for oxidizing agents

11.11 Sodium Hydroxide (0.25N)

11.11.1 Dissolve 10.0 g of sodium hydroxide pellets in a 1000 mL volumetric half-filled with reagent water. After all the material has dissolved, fill to the mark with reagent water.

11.11.2 Store tightly sealed in a labeled, inert polyethylene bottle at room temperature. Expiration is 6 months from the date made.

11.12 Bismuth Nitrate (0.026M)

11.12.1 Dissolve 30.0 g of $Bi(NO_3)\cdot 5H_2O$ in 100 mL laboratory reagent water, in a 1 L volumetric. While stirring, add 250 mL of glacial acetic acid. Stir until the material has dissolved. Dilute to 1 L with laboratory reagent water. Store tightly sealed in a labeled, inert polyethylene bottle at room temperature. Expiration is 6 months from the date made.

11.13 Magnesium Chloride (2.5M)

11.13.1 Dissolve 510 g of $MgCl_2\cdot 6H_2O$ in a 1 L volumetric half-filled with reagent water. After all the material has dissolved, fill to the mark with reagent water. Store tightly sealed in a labeled, inert polyethylene bottle at room temperature. Expiration is 6 months from the date made.

11.14 Sulfamic Acid Solution (0.4N)

11.14.1 Dissolve 40 g of NH_2SO_3H in a 1 L volumetric half-filled with reagent water. After all the material has dissolved, fill to the mark with reagent water. Store tightly sealed in a labeled, inert polyethylene bottle at room temperature. Expiration is 6 months from the date made.

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11.15 Glacial Acetic Acid (CH_3COOH), EM Omnitrace™ or equivalent

11.16 Anhydrous Sodium Acetate (CH_3COONa), ACS grade or better

11.17 Acetate Buffer Solution (pH = 4.0)

11.17.1 Dissolve 7.3 g of CH_3COONa in a 50 mL volumetric filled with about 20 mL of reagent water. Add 24 g of CH_3COOH (glacial) and swirl to mix. After all the material has dissolved, fill to the mark with reagent water. Store tightly sealed in a labeled, inert polyethylene bottle at room temperature. Expiration is 6 months from the date made.

Note: Check and record the solution pH after making.

11.18 Antifoam, silicone emulsifying agent

12.0 STANDARDS PREPARATION

12.1 Any samples treated with bismuth nitrate for sulfide interference (Section 13.18) must be quantitated using a calibration curve treated with bismuth nitrate.

12.2 Calibration standards preparation is covered in TriMatrix SOP GR-05-122, Section 12.0.

13.0 ANALYTICAL PROCEDURE

13.1 Water and wastewater samples must be homogenized by shaking just before removing a sample aliquot for analysis. After shaking well, measure 50 mL of sample with a graduated cylinder. Transfer the aliquot to a distillation tube containing 2 or 3 boiling chips.

13.2 Check each aliquot for sulfides with lead acetate paper. A black color on the paper indicates sulfides are present and the sample must be treated using bismuth nitrate (Section 13.18). If treated, a bismuth nitrate calibration must be used for quantitation.

13.3 Check each aliquot for oxidizing agents with potassium iodide starch paper (dampened with acetate buffer). A blue color on the paper indicates oxidizing agents are present. Add approximately 0.2 g of L-ascorbic acid. Stir and test again. Repeat until the paper no longer turns blue then add approximately 0.05 g more L-ascorbic acid powder.

13.4 Position the distillation tube containing the sample aliquot into the left rear position of the midi-distillation block.

13.5 Add 50 mL of 0.25N NaOH to a scrubber/absorber tube and place in the front left position of the block. If a sample appears foamy, add 1 to 2 drops of antifoam before starting the distillation.

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Note: If antifoam is used, the distillation blank (BLK) and blank spike (BS) must also use antifoam.

13.6 Place a reflux impinger with the gas exit tube facing the rear of the block into the distillation tube.

13.7 Place an absorber impinger with the gas inlet tube facing the rear of the block into the scrubber/absorber tube.

13.8 Connect the absorber impinger gas inlet tubing to the reflux impinger gas outlet.

13.9 Connect the absorber impinger vacuum tubing to the vacuum outlet.

13.10 Place a Cold-Finger Condenser, with water ports facing the rear of the block, into the reflux impinger.

13.11 Connect Cold-Finger Condenser water tubing to the water manifold quick-disconnect adapters on the rear of the block. The lower tubing connects to the left front quick-disconnect adapter (water outlet) and the upper tubing connects to the left rear quick-disconnect adapter (water inlet).

13.12 Repeat Sections 13.1 through 13.11 for each sample, moving from left to right across the block. Up to 10 samples may be loaded at one time.

13.13 Turn off all vacuum valves.

13.14 Check to make sure an excess gas trap is loaded and connected to the vacuum line attached to the block.

13.15 Turn on the cooling water and adjust to 6 gal/hr for each distilling position. For example, if 4 samples are being distilled, adjust the flow to 24 gal/hr (6 x 4 = 24 gal/hr).

Note: NEVER operate the cooling water unless cold-finger condensers are connected to the water manifold. Improper use may damage cold-finger condensers and/or rupture the tubing.

13.16 Turn on the vacuum and adjust each valve to give a flow of three bubbles per second in each reflux tube.

13.17 Let the vacuum draw for 5 minutes.

13.18 If a sample tested positive for sulfide (Section 13.2), add 10 mL bismuth nitrate solution at this time.

13.19 Add 5 mL of sulfamic acid through the air inlet of each reflux impinger.

13.20 Inject 5 mL of 1:1 (v/v) sulfuric acid through the air inlet of each reflux impinger.

13.21 Let the vacuum draw for 5 minutes more.

13.22 Inject 2 mL of magnesium chloride solution through the air inlet of each reflux impinger.

13.23 Turn the distillation block on. The red rocker switch light will glow while the unit is on.

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13.24 Turn on the timer. The green timer light and amber heat lights will glow. The timer is set for 15 minutes of heat-up and 90 minutes of distilling. The distilling block temperature is preset to 125° C.

13.25 The timer will automatically turn off the heating block when the time has expired. Vacuum draw and cooling water are unaffected by turning the heat off.

13.26 Let the distilling block cool for 15 minutes before turning off the cooling water and vacuum.

13.27 Close each valve and disconnect the absorber gas inlet tubing from the reflux impinger.

13.28 Starting from the right, open the valve to draw all solution from the absorber impinger frit. Close the valve and remove the impinger frit.

13.29 Disconnect the impinger vacuum tubing and remove the absorber impinger from the unit.

13.30 Pour the scrubber solution from the absorber tube into a plastic specimen cup. Label and tightly cap the specimen cup until analysis, which must be within the sample holding time.

13.31 Working from right to left, repeat Sections 13.28 through 13.30 for each distilling position.

14.0 DATA REPORTING AND DELIVERABLES

14.1 Record the following data on the preparation batch report for each sample batch distilled:

14.1.1 Sample volume distilled, in mL

14.1.2 Final volume of diluted scrubber/absorber solution

14.1.3 Volume and concentration of all stock standards used as spikes

14.1.4 Analyst initials

14.1.5 Date

14.2 Refer to Attachment 20.2 for a preparation batch report/analysis sequence example.

15.0 QUALITY ASSURANCE

15.1 Method and matrix QC must be distilled with each sample analysis batch. A batch consists of up to 20 samples per matrix and may be left open for up to 14 days.

15.1.1 A blank spike (BS) is an aliquot of reagent water spiked from a stock standard, which is distilled and analyzed like a sample. Distill a low and high range BS with each batch.

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15.1.1.1 To prepare a high-concentration blank spike, measure and transfer 50 mL of reagent water into a distillation tube. Pipet 50 µL of the 100 mg/L stock standard (Refer to Section 12.7 of TriMatrix SOP GR-05-122) then proceed with the distillation and analysis. The high-range BS concentration is 0.1 mg/L cyanide.

15.1.1.2 To prepare a low-concentration BS, measure and transfer 50 mL of reagent water into a distillation tube. Pipet 20 µL of the 100 mg/L stock standard (Refer to section 12.7 of TriMatrix SOP GR-05-122) then proceed with the distillation and analysis. The low-range BS concentration is 0.04 mg/L cyanide.

15.1.2 A method blank (BLK) is 50 mL of reagent water distilled and analyzed like a sample. Measure and transfer 50 mL of reagent water to a distillation tube then proceed with the distillation and analysis.

15.1.3 At a minimum, a low-range blanks spike, a high-range blank spike and method blank are distilled at the start of every batch. Until a batch is closed (at 20 samples or in 14 days), a low-range BS and BLK <u>or</u> a high-range BS and BLK must also be distilled with each distillation set processed into the open batch. Consequently, BS/BLK data within each batch will vary with the number of times midi-distillation is performed before the batch is closed.

Note: Place QC samples in the Midi-block randomly. Do not use the same position to run QC for each batch.

15.1.4 Acceptance limits for quality control are listed in the laboratory information management system (Element™).

15.2 Matrix QC consists of replicate matrix spikes, labeled MS and MSD. Matrix spikes are performed at a frequency of one set per batch of up to 20 samples per matrix.

15.2.1 To prepare a matrix spike/matrix spike duplicate, measure and transfer two 50 mL sample aliquots into two separate distillation tubes. Pipet 50 uL of the 100 mg/L stock standard (Refer to Section 12.7 of TriMatrix SOP GR-05-122) then proceed with the distillation and analysis. The matrix spike concentration is 0.1 mg/L.

15.2.2 If sample concentration is high, sample dilution and adjustment to the spike quantity may be necessary.

15.2.3 Acceptance limits for matrix quality control are listed in the laboratory information management system (Element™).

15.3 All corrective action in association with out-of-control quality control must be in accordance with TriMatrix SOP GR-10-106.

16.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

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16.1 Before actual sample analysis, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC). While IDCs are not instrument dependent, one is required on each instrument used in sample distillation or analysis, to demonstrate the instrument's ability to generate acceptable accuracy and precision. Annually, a Continuing Demonstration of Capability (CDC) is required.

16.1.1 Initial Demonstration of Capability

16.1.1.1 Prepare four aliquots of laboratory reagent water spiked with second-source stock standard. Distill and analyze the four prepared spikes following every step outlined in both distillation and analysis procedures. Use the IDC spreadsheet on the intranet library to calculate average percent recovery from the results obtained and relative standard deviation of the average. Recovery must be within 90 - 110% for drinking water samples and within blank spike acceptance limits for all other matrices. Relative standard deviation must be ≤20%.

16.1.1.2 If either criterion fails, locate and correct the source of the problem and repeat the study. Repeated failure however, will confirm a general problem with the procedure or techniques used. If this occurs, locate and correct the source of the problem, revise the procedure or techniques used and repeat the study. Samples may not be analyzed by any analyst or on any instrument until a demonstration of capability study has been successfully completed.

16.1.1.3 Copies of all (successful and unsuccessful) IDC/Method Validation spreadsheets and raw data must be submitted to Quality Assurance for training documentation.

16.1.2 Continuing Demonstration of Capability (CDC)

16.1.2.1 A CDC must be performed annually by all analysts distilling samples for cyanides analysis.

16.1.2.2 The CDC may be completed by one of the following approaches:

16.1.2.2.1 By repeating the IDC study

16.1.2.2.2 By distilling an acceptable PE sample during the course of routine sample analysis

16.1.2.2.3 By using the last four results from an MDL study distilled during the course of routine sample analysis.

Note: In each case, the work must have been done exclusively by one analyst.

16.2 A Method Detection Limit (MDL) Study must be completed annually in accordance with TriMatrix SOP GR-10-125.

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17.0 POLLUTION PREVENTION

17.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

17.2 Never dispose of laboratory chemicals without first referencing appropriate written instructions of disposal for that particular material.

17.3 Conserve the use of chemicals where applicable.

17.4 Comply with all environmental laws associated with chemicals in the laboratory.

18.0 WASTE MANAGEMENT

18.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals. Material safety data sheets are available on the laboratory intranet library.

18.2 To minimize the environmental impact and costs associated with chemical disposal, order and use only the minimum amount of material required.

18.3 Follow all instructions in TriMatrix SOP GR-15-102 for laboratory waste disposal requirements.

19.0 REFERENCES

19.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update IV, Revision 3, November 2004, Method 9010C, "Total and Amenable Cyanide Distillation"

19.2 *Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1995,* 4500-CN⁻ B, Cyanide, Preliminary Treatment of Samples

19.3 *Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1995,* 4500-CN⁻ C, Cyanide, Total Cyanide after Distillation

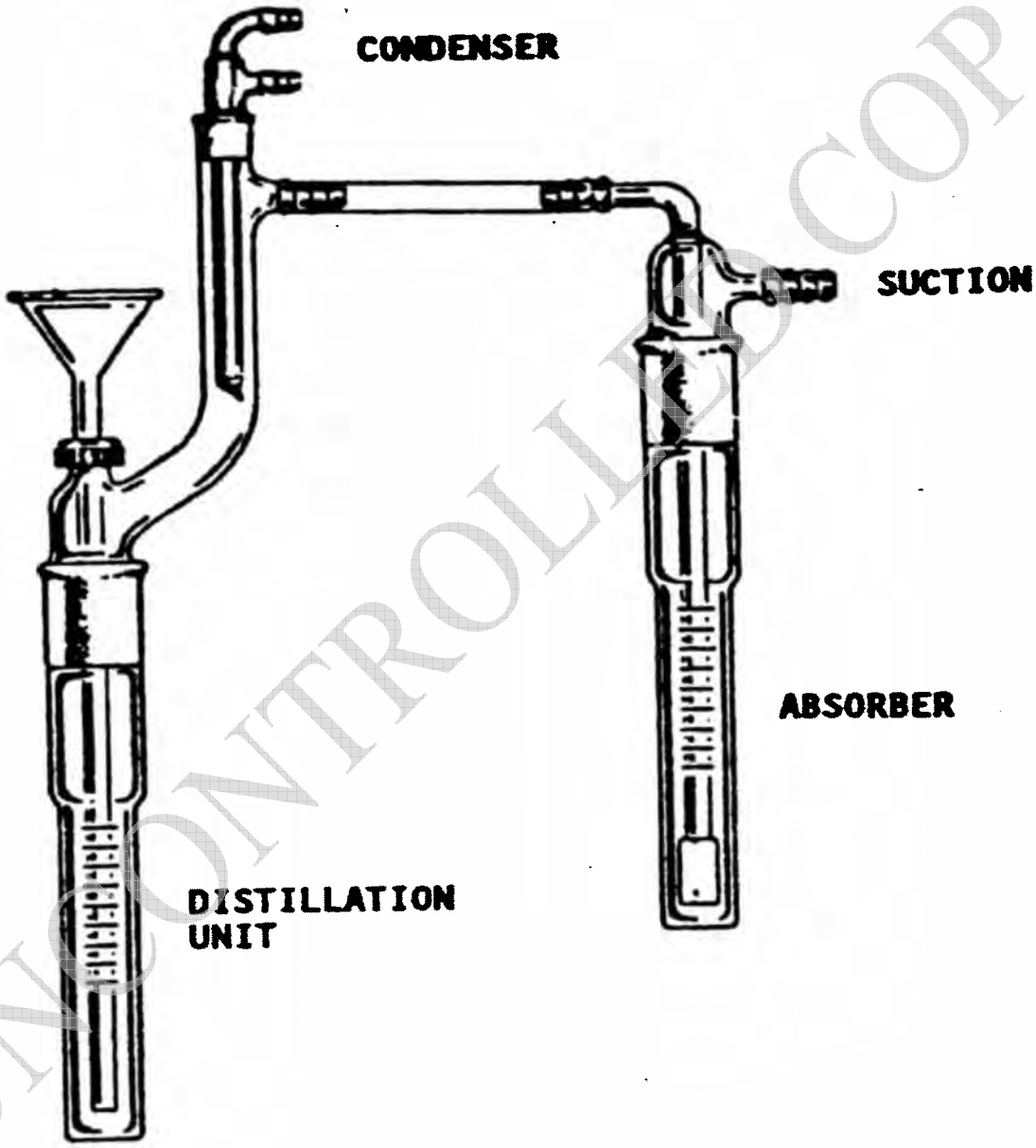
20.0 ATTACHMENTS

20.1 Reflux Distillation Apparatus

20.2 Preparation Batch Report Example

Approved By: 11-13-09 **QA Officer** **Approved By:** Heather L. Brady **Area Supervisor**

Attachment 20.1
Reflux Distillation Apparatus



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Attachment 20.2
Pre-treatment Benchsheet Example

TriMatrix Laboratories, Inc. **PREPARATION BATCH** 0911292 Page 1 of 1 Printed: 9/28/2009 2:55:22PM

Inorganic - Wet Chemistry, Waste Water, 4500-CN C Cyanide Distillation

(No Surrogate)

Batch Comments: (none)

Work Order	Analysis	Work Order	Analysis	Work Order	Analysis
0909471	Cyanide, Total 335.4				

Lab Number	Contain	Prepared	By	Initial (mL)	Final (mL)	uL Surrogate	Source ID	Spike ID	uL Spike	Client / QC Type	Extraction Comments
0911292-BLK1		Sep-25-09 06:00	LMA	50	50					BLANK	
0911292-DUP1		Sep-25-09 06:00	LMA	50	50		0909471-04			DUPLICATE	
0911292-BS1		Sep-25-09 06:00	LMA	50	50			9090699	50	LCS	
0911292-BS2		Sep-25-09 06:00	LMA	50	50			9090699	20	LCS	
0911292-MS1		Sep-25-09 06:00	LMA	50	50		0909471-04	9090699	50	MATRIX SPIKE	
0909471-01	B	Sep-25-09 06:00	LMA	50	50					[redacted]	
0909471-02	B	Sep-25-09 06:00	LMA	50	50					[redacted]	
0909471-03	B	Sep-25-09 06:00	LMA	50	50					[redacted]	
0909471-04	B	Sep-25-09 06:00	LMA	50	50					[redacted]	
0909471-05	B	Sep-25-09 06:00	LMA	50	50					[redacted]	

Comments:	Analyst Initials

bch_TriMatrix.rpt

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Approved By: 11-13-09 **QA Officer** **Approved By:** Heather L Brady **Area Supervisor**

TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

Total Cyanide by Konelab UV Spectrophotometry

Standard Methods 4500-CN G
Standard Methods 4500-CN E
SW-846 Method 9014

APPROVALS:

Area Supervisor: Heather L. Brady Date: 9-15-09
Heather L. Brady

QA Officer: Date: 9-10-09
Tom C. Boocher

Operations Manager: Date: 9/14/09
Jeff P. Glaser

Procedure Number: GR-05-122
Revision Number: 0.4

Date Initiated: 10/28/03
Effective Date: 9/25/09

Date Revised: 9/10/09
Pages Revised: All

By: Jodi L. Blouw

Total Number of Pages: 18

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

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1.0 SCOPE AND APPLICATION

1.1 This procedure is applicable to the determination of cyanide in drinking and surface waters, domestic and industrial wastes, and soil.

1.2 The applicable range for water samples is 0.005 mg/L to 0.20 mg/L.

1.3 The reporting limit for water samples is 0.005 mg/L. The reporting limit for soils is 0.2 mg/kg.

2.0 PRINCIPLE PROCEDURE REFERENCES

2.1 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, 4500-CN⁻ E, "Colorimetric Method"

2.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, 4500-CN⁻ G, "Cyanides Amenable to Chlorination after Distillation"

2.3 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,* SW-846, 3rd Edition, Final Update III, Revision 0, December, 1996, Method 9014, "Titrimetric and Manual Spectrophotometric Determinative Methods for Cyanide"

3.0 SUMMARY OF PROCEDURE

3.1 Cyanide in alkaline distillate is converted to cyanogen chloride (CNCl) by reaction with chloramine-T below pH 8.0, without hydrolyzing to CNO^{1-}.

3.2 CNCl then forms a red-blue color by reacting with pyridine-barbituric acid. The developed color is read at 575 nm on the Konelab spectrophotometer.

Note: The methods are modified by replacing 0.04N sodium hydroxide (NaOH) diluent with 0.25N NaOH to maintain the same NaOH concentration between manual and automated distillation.

4.0 PARAMETER OR COMPOUND LIST

4.1 Total Cyanide

4.2 Amenable Cyanide

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-18-106, *Cyanide Total, Preliminary Macro-Distillation from Soil, Sludge and Waste,* latest revision

5.2 TriMatrix SOP GR-18-109, *Cyanide, Preliminary Midi-Distillation*, latest revision

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5.3 TriMatrix SOP GR-10-106, *Inorganic and Metals Laboratories Corrective Actions*, latest revision

5.4 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal,* latest revision

5.5 TriMatrix SOP GR-10-125, *Method Detection Limit (MDL)*, latest revision

5.6 TriMatrix SOP GR-05-129, *Konelab 20 Operation*, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Distillation removes most interferences. Refer to TriMatrix SOP GR-18-106 and GR-18-109 for distillation procedures.

7.0 SAFETY PRECAUTIONS

7.1 Wear a laboratory coat and approved safety glasses while in the laboratory. In addition, disposable gloves must be worn whenever samples or reagents are handled.

7.2 Follow all instructions outlined in the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan.

7.3 For laboratory waste disposal, refer to TriMatrix SOP GR-15-102.

7.4 The total toxicity and/or carcinogenicity of reagents used in this procedure have not been precisely defined.

7.4.1 Treat all chemicals as a potential health hazard.

7.4.2 Reduce exposure to the lowest possible level by adherence to established safety policies.

7.4.3 Material Safety Data Sheets are maintained on the laboratory intranet of all chemicals used in this procedure. Consult the MSDS for detailed chemical information.

7.5 Samples can be highly toxic and varied. Treat any exposure as a potential danger and immediately decontaminate the exposure. Clean waste-contaminated personal protective equipment before using again.

7.6 Bring all safety issues to the attention of the Area Supervisor and/or Health and Safety Officer.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Water and wastewater samples are collected in opaque brown plastic bottles. Samples are preserved with sodium hydroxide to greater than pH 12.

8.2 Wastes, sludge and soils are collected in glass jars without preservative.

8.3 Samples must be stored at 4 ±2° C until analysis.

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8.4 Homogenize water samples by shaking immediately before removing a sample aliquot. Wastes, sludge and soils must be homogenized using an appropriate mixing procedure, before distillation.

8.5 Distillation and analysis must be performed within 14 days of sample collection.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Konelab Aqua 20 automated UV spectrophotometer, Type 968, at 575 nm. Refer to the Equipment List located on the laboratory intranet library for a full description of minimum and current instrument specifications.

9.2 Volumetric flasks, various sizes

9.3 Pipets:

9.3.1 Volumetric, glass, type A

9.3.2 Micropipette, calibrated and serialized

9.3.3 Macropipette, calibrated and serialized

9.4 Personal computer. Refer to the Information Technology (IT) department's Computer Inventory Database for minimum and current computer and software specifications associated with the analytical instrument.

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Refer to TriMatrix SOP GR-05-129 for a schedule of preventive instrument maintenance.

11.0 CHEMICALS AND REAGENTS

11.1 Indicator solution: Dissolve 0.020 g p-dimethylaminobenzal-rhodanine in 100 mL acetone. Expiration for this solution is six months from the date made.

11.2 Indicator solution: Potassium chromate (K_2CrO_4), 5% (w/v), Purchased commercially.

11.3 Sodium Chloride Standard: Dissolve 1.125 g NaCl (dried at 140° C) in reagent water. Dilute to 1000 mL with reagent water. Expiration for this solution is six months from the date made.

11.4 Silver nitrate titrant: Dissolve 3.27 g $AgNO_3$ in 1 L reagent water. Standardize against the NaCl standard, using the argentometric titration, with K_2CrO_4 indicator. Expiration for this solution is six months from the date made.

$$Cl^- + AgNO_3 \xrightarrow{K_2CrO_4} AgCl(s) + NO_3$$

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$$2Ag^{+} + CrO_4^{2-} \longrightarrow Ag_2CrO_4$$

11.4.1 $AgNO_3$ Standardization:

11.4.1.1 Place 10.0 mL of the NaCl standard and about 100 mL of reagent water, into a beaker.

11.4.1.2 Add 1 mL K2CrO4 indicator solution.

11.4.1.3 Titrate with $AgNO_3$ solution, to a pinkish yellow endpoint.

11.4.2 The $AgNO_3$ correction factor is calculated as follows:

$$\frac{A}{B} = C$$

Where:
A = NaCl standard volume, in mL
B = $AgNO_3$ titrant used, in mL
C = Correction factor

11.5 Laboratory Reagent Water: ASTM Type II, Milli-Q system

11.6 Chloramine-T solution: Dissolve 1.0 g chloramine T in 100 mL reagent water. Prepare weekly and store at 4 ±2° C in the refrigerator.

11.7 Sodium dihydrogen phosphate buffer, 1M: Dissolve 34.5 g $NaH_2PO_4 \cdot H_2O$ in 250 mL of laboratory reagent water. Expiration for this solution is six months from the date made. Store at 4 ±2° C in the refrigerator.

11.8 Pyridine-barbituric acid reagent:

11.8.1 Weigh 15.0 g barbituric acid in a 250 mL volumetric flask. Add just enough water to wash down the flask neck and wet the barbituric acid.

11.8.2 Add 75 mL pyridine. Cap and mix.

11.8.3 Add 15 mL concentrated hydrochloric acid (HCl). Mix and cool to room temperature. Dilute to the mark with reagent water, and mix again.

11.8.4 This reagent is stable for up to six months. Discard if a precipitate forms. Prepare in a hood. Store at 4 ±2° C in the refrigerator.

11.9 Sodium Hydroxide Diluent (0.25 N):

11.9.1 In a 2 L volumetric flask, dissolve 20.0 g sodium hydroxide in 1000 mL reagent water.

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11.9.2 Dilute to 2000 mL. Invert several times to mix.

11.9.3 The solution may be stored in an inert plastic bottle at room temperature, for up to six months.

11.10 All reagents must be recorded in the reagents log with a unique ID number. Refer to Attachment 23.1 for a reagents log example.

12.0 STANDARDS PREPARATION

12.1 Primary Cyanide Solution (1000 mg/L CN^-):

12.1.1 Cyanide solutions are prepared from ACS stock.

12.1.2 Dissolve 1.255 g potassium cyanide and 1.0 g potassium hydroxide in 400 mL of reagent water, in a 500 mL volumetric flask. Dilute to volume with reagent water. The concentration is 1000 mg/L cyanide. Expiration for this solution is six months from the date made.

12.1.3 This standard must be re-standardized by titration, weekly.

CAUTION: KCN is highly toxic. Avoid inhalation of cyanide dust, or contact with the solid or solutions.

12.2 Standardize the 1000 mg/L CN^- solution as follows:

12.2.1 Dilute 10 mL of the 1000 mg/L KCN to 100 mL, using 0.25N NaOH diluent.

12.2.2 Add 0.5 mL of rhodanine indicator.

12.2.3 Titrate with standardized $AgNO_3$ solution to the first color change from a canary yellow to a salmon hue.

12.2.4 Titrate a 0.25N NaOH blank.

12.2.5 Cyanide concentration in the standard is calculated as follows:

$$\frac{\text{mg CN -}}{\text{L}} = (A-B) \times 100 \times C$$

Where:
A = $AgNO_3$ titrant used for the standard, in mL
B = $AgNO_3$ titrant used for the blank, in mL
C = $AgNO_3$ titrant correction factor (from section 11.4.2)

12.3 Intermediate Cyanide Solution (100 mg/L CN^-):

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12.3.1 Prepare a 100 mg/L CN^- standard by measuring the appropriate calculated volume of 1000 mg/L CN^- solution into a 100 mL volumetric flask.

12.3.2 Dilute to volume with 0.25N NaOH.

12.3.3 Expiration for this solution is one week from the date made.

12.4 Tertiary Cyanide Solution (1.0 mg/L CN^-):

12.4.1 Prepare a 10 mg/L CN^- solution by measuring 10 mL of 100 mg/L CN^- into approximately 60 mL of 0.25N NaOH in a 100 mL volumetric flask.

12.4.2 Dilute to volume with 0.25N NaOH. The concentration is 10 mg/L. Prepare fresh daily.

12.4.3 Then, prepare a 1.0 mg/L CN^- standard by measuring 10 mL of 10 mg/L CN^- into approximately 60 mL of 0.25 N NaOH in a 100 mL volumetric flask.

12.4.4 Dilute to volume with 0.25N NaOH. The concentration is 1.0 mg/L CN^-. Prepare fresh daily.

12.4.5 Use to prepare the calibration.

12.5 Calibration Standards are prepared as follows (prepare fresh daily):

Concentration mg/L	**Dilution**
0.2	20 mL 1.0 mg/L CN^- to 100 mL, with 0.25 N NaOH
0.1	10 mL 1.0 mg/L CN^- to 100 mL, with 0.25 N NaOH
0.05	5.0 mL 1.0 mg/L CN^- to 100 mL, with 0.25 N NaOH
0.02	10 mL 0.2 mg/L CN^- to 100 mL, with 0.25 N NaOH
0.01	10 mL 0.1 mg/L CN^- to 100 mL, with 0.25 N NaOH
0.005	10 mL 0.05 mg/L CN^- to 100 mL, with 0.25 N NaOH

12.6 Prepare a second-source 1000 mg/L cyanide standard with KCN reagent purchased from an alternate vendor according to Section 12.1.

12.6.1 Standardize as in Section 12.2.

12.6.2 Prepare an intermediate dilution then 0.05 mg/L and 0.1 mg/L working standards (Sections 12.3 through 12.5).

12.6.3 Use these working standards as the second-source calibration verification (SCV).

12.6.4 Refer to Section 18.2.2 for SCV acceptance limits.

12.7 Record all standard preparations in the appropriate standards log in Element™ with a unique ID number. Refer to Attachment 23.2 for a standards log example.

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12.8 Primary and secondary cyanide standards must be labeled with the following information:

12.8.1 Initials of the preparer

12.8.2 Preparation date

12.8.3 Concentration, with units

12.8.4 Parameter name

12.8.5 Standards logbook number as it appears in the standards logbook

12.8.6 Diluted volume

12.9 Working standards must be labeled with the following information:

12.9.1 Initials of the preparer

12.9.2 Preparation date

12.9.3 Concentration, with units

12.9.4 Parameter name

12.9.5 Expiration date

12.9.6 Standards logbook number as it appears in the standards logbook

13.0 SAMPLE PREPARATION

13.1 All samples must be distilled before analysis.

13.2 Refer to TriMatrix SOP GR-18-106 and TriMatrix SOP GR-18-109 for distillation instructions.

14.0 CALIBRATION PROCEDURES

14.1 Analyze working calibration standards (Section 12.5) in increasing order. Analyze by Section 15.0 instructions to obtain absorbance readings.

14.2 The instrument will generate a calibration curve of absorbance vs concentration, with the best-fit linear regression line through the data. Do not force through the origin or set the instrument to use non-linear spline functions as cyanide response is a linear calibration.

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14.2.1 Linear regression curves are constructed by the instrument using concentration plotted against absorbance. The following equation is a linear regression calculation to determine sample concentrations.

$X_S = (Y_S - b)/m$

Where:
Ys = Absorbance in sample "s"
Xs = Concentration of cyanide in sample "s"
m = Slope "s" of the calibration curve
b = The y-intercept of the calibration curve

14.2.2 Refer to Attachment 23.3 for an example cyanide calibration curve.

15.0 ANALYTICAL PROCEDURE

15.1 Turn on the Konelab spectrophotometer.

15.2 Select "cyanide" as the run method

15.3 Fill sample cups with the appropriate standards and sample distillates. Place in the instrument.

15.4 For color development, the Konelab performs the following:

15.4.1 Takes 100 µL from the sample cup.

15.4.2 Adds 20 µL phosphate buffer.

15.4.3 Adds 4 µL chloramine-T solution, then incubates for 2 minutes at 37° C.

15.4.4 The instrument then takes a background reading before adding 10 µL of pyridine–barbituric acid solution.

15.5 Absorbance is measured by the spectrophotometer at 575 nm, 10 minutes after adding the pyridine - barbituric acid.

15.6 When analysis is complete, perform a Konelab shut-down and turn the instrument off.

16.0 CALCULATIONS AND DATA HANDLING

16.1 The Konelab regresses all data against the calibration curve then prints out concentration and absorbance. The analyst need only account for dilutions. Refer to Attachment 23.3, for a Konelab calibration and run data example.

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17.0 DATA REPORTING AND DELIVERABLES

17.1 The following must be attached to laboratory benchsheets for each batch analyzed:

17.1.1 Spectrophotometer raw data hardcopy

17.1.2 Calibration curve printout

17.1.3 Batch detail report

17.2 The instrument logbook (Refer to Attachment 23.4) must be filled in for each batch analyzed with the following information:

17.2.1 Date analyzed

17.2.2 Analyst initials

17.2.3 Method name

17.2.4 Calibration standards used

17.2.5 Client name and sample numbers analyzed

17.3 The following data must be recorded in the batch detail report (Refer to Attachment 23.5) for each batch analyzed:

17.3.1 BS, MPB, SCV, BLK, CCV, CCB, SPK, MSD or DUP results. Sample concentration, with units.

17.3.2 Instrument number, date run, supervisor, stock standard number, wavelength, cell path.

17.3.3 Standard concentrations with units, observed standard concentrations, working standard ID numbers.

18.0 QUALITY ASSURANCE

18.1 Method and matrix quality control (QC) must be analyzed for each analysis batch.

18.2 Method QC consists of a Blank Spike (BS), two second-source calibration verifications (SCV), a Distillation Blank (BLK), an Instrument Blank (BLK), Continuing Calibration Blanks (CCB) and Continuing Calibration Verifications (CCV).

18.2.1 The BS is a known concentration of cyanide standard spiked into 0.25 N NaOH diluent. Concentration is 0.04 mg/L or 0.1 mg/L. Spike, then distill and analyze as a sample. Acceptance limits must be between 90 and 110% for drinking water samples and within limits listed in the laboratory information management system (Element™) for other matrices.

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18.2.2 The SCV is a known concentration of second-source cyanide standard spiked into 0.25 N NaOH and analyzed like a sample. Prepare two SCVs as described in Section 12.6. Percent recovery must be between 90 and 110% for drinking water samples and within limits listed in the laboratory information management system (Element™) for other matrices.

18.2.3 The distillation BLK is an aliquot of laboratory reagent water, distilled and analyzed as a sample. The result must be less than the reporting limit.

18.2.4 The instrument blank BLK is an aliquot of 0.25N NaOH analyzed as a sample but without distillation. The result must be less than the reporting limit.

18.2.5 The CCV is an aliquot of midrange standard analyzed immediately after the calibration curve has been confirmed, after every 10 samples and at the end of the analytical run.

18.2.5.1 CCV acceptance limits are 90 to 110% of the expected value.

18.2.5.2 Include in the ten-sample CCV count the BS, SCV, BLK, MS, MSD and DUP runs.

18.2.6 The CCB is an aliquot of 0.25N NaOH analyzed immediately after the CCV. The result must be less than the reporting limit.

18.3 Matrix QC consists of a matrix pikes (MS) and matrix spike duplicate (MSD).

18.2.1 Two sample aliquots are spiked with a known cyanide concentration then distilled and analyzed in the same way as the unspiked sample.

18.2.2 Acceptance limits for recovery are listed in Element™.

18.2.3 Calculate SPK1/SPK2 duplication as relative percent difference (RPD). The maximum RPD limit is listed on the cyanides benchsheet.

18.4 Refer to TriMatrix SOP GR-10-106 for corrective action on unacceptable quality control results.

19.0 ANALYST CERTIFICATION/METHOD VALIDATION

19.1 Before actual sample analysis, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC) study. While IDCs are not instrument dependent, one is required on each instrument to demonstrate the instrument's ability to generate acceptable accuracy and precision.

19.1.1 Initial Demonstration of Capability (IDC) Study

19.1.1.1 Prepare and analyze four aliquots of SCV following every step in the distillation and analysis.

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19.1.1.2 Input the four results to the IDC spreadsheet located on the laboratory intranet library to calculate average percent recovery and relative standard deviation (%RSD).

19.1.1.3 Average recovery must be 90 - 110%. Relative Standard deviation must be less than or equal to 20%.

19.1.1.4 If either criterion is not met, locate and correct the source of the problem and repeat the study successfully.

19.1.1.5 Repeated failure will indicate a general problem with the procedure and/or techniques used. If this occurs, locate the problem, correct the procedure and/or techniques used then repeat the study successfully.

19.1.1.6 Samples may not be analyzed by any analyst or on any instrument until a demonstration of capability study has been successfully completed.

19.1.1.7 Give a copy of the successful IDC spreadsheet and data to Quality Assurance for training documentation.

19.1.2 Continuing Demonstration of Capability (CDC) Study

19.1.2.1 A CDC study must be performed annually by all analysts running this procedure.

19.1.2.2 The CDC may be accomplished by any one of the following approaches:

19.1.2.2.1 By repeating the IDC study

19.1.2.2.2 By using four consecutive SCV results run exclusively by the analyst obtained during the course of routine sample analysis

19.1.2.2.3 By exclusively running and successfully passing a blind cyanide PT sample during the course of routine sample analysis.

19.1.2.2.4 By using the last four of seven results obtained from an MDL study run exclusively by the analyst. ONLY the last four results may be used.

19.1.2.3 Give a copy of the successful CDC spreadsheet and data to Quality Assurance for training documentation.

19.2 A method detection limit study must be run annually in accordance with TriMatrix GR-10-125.

20.0 POLLUTION PREVENTION

20.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

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20.2 Never dispose of laboratory chemicals without first referencing appropriate written instructions of disposal for that particular material.

20.3 Conserve the use of chemicals where applicable.

20.4 Comply with all environmental laws associated with chemicals in the laboratory.

21.0 WASTE MANAGEMENT

21.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals. These documents are located on the laboratory intranet library.

21.2 To minimize the environmental impact and costs associated with the disposal of chemicals, order and use only the minimum amount of material required.

21.3 Follow all instructions in TriMatrix SOP GR-15-102 for laboratory waste disposal requirements.

22.0 REFERENCES

22.1 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, 4500-CN⁻ E, "Colorimetric Method"

22.2 Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1998, 4500-CN⁻ G, "Cyanides Amenable to Chlorination after Distillation"

22.3 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,* SW-846, 3rd Edition, Final Update III, Revision 0, December, 1996, Method 9014, "Titrimetric and Manual Spectrophotometric Determinative Methods for Cyanide"

23.0 ATTACHMENTS

23.1 Reagents Log Example

23.2 Standards Log Example

23.3 Spectrophotometer Calibration and Run Data Example

23.4 Instrument Logbook Example

23.5 Batch Detail Report Example

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Attachment 23.1
Reagent Log Example

Analytical Standard Record
TriMatrix Laboratories, Inc.
7010874

Description:	Potassium phosphate USP Dibasic	Expires:	Aug-16-11
Standard Type:	Reagent	Prepared:	Aug-16-06
Solvent:	Solvent Lot #	Prepared By:	** Vendor **
Final Volume (mls):	500	Department:	Inorganic - Wet Chemistry
Vials:	1	Last Edit:	Feb-01-07 16:07 by TCB

Fisher part#P290-500
Lot 064412
Received 1/29/07

Analyte	CAS Number	Concentration	Units
			NA

Reviewed By _____ Date _____

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Approved By: M 9-10-09 **QA Officer** **Approved By:** Heather L. Brady **Area Supervisor**

Attachment 23.2
Standards Log Example

Analytical Standard Record
TriMatrix Laboratories, Inc.
7050855

Description:	Potassium Cyanide	Expires:	Feb-05-12
Standard Type:	Reagent	Prepared:	Feb-05-07
Solvent:	Solvent Lot #E04793	Prepared By	** Vendor **
Final Volume (mls):	125	Department:	Inorganic - Wet Chemistry
Vials:	1	Last Edit:	May-25-07 14:46 by TCB

JT Baker part# 3080-04
Lot: E04793
Received 5/24/07

Analyte	CAS Number	Concentration	Units
			NA

Reviewed By Date

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Approved By: 9-10-09 **QA Officer** **Approved By:** Heather L. Brady **Area Supervisor**

Attachment 23.3
Spectrophotometer Calibration and Run Data Example

Calibration results — Konelab 6.0.2 — Page: 1

Trimatrix
Analyst:

15.01.2004 11:11

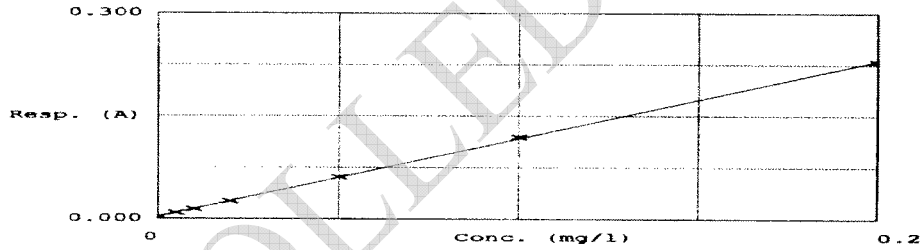
Test Cyanide

Accepted 15.01.2004 08:47

Factor 0.879
Bias 0.003

Coeff. of det. 0.999829

Errors



	Calibrator	Response	Calc. con.	Conc.	Errors
1	CN-0	0.003	-0.00052	0.00000	
2	CN-0.005	0.009	0.00473	0.00500	
3	CN-0.01	0.014	0.00957	0.01000	
4	CN-0.02	0.026	0.01975	0.02000	
5	CN-0.05	0.061	0.05066	0.05000	
6	CN-0.10	0.119	0.10184	0.10000	
7	CN-0.20	0.230	0.19897	0.20000	

Result Report — Konelab 6.0.2 — Page: 1

Trimatrix
Analyst:

Date : 2004-01-15
Time : 11.11

Test Cyanide
Unit mg/l

Sample ID:	Result	Date and Time	Man.dilut	Dilut
CNicv/ccv	0.0950	2004-01-15 09.05		
CNicb/ccb	0.0002	2004-01-15 09.05		
blk	0.0003	2004-01-15 09.05		
lcs 0.1	0.0999	2004-01-15 09.05		
lcs 0.05	0.0488	2004-01-15 09.05		
crdl	0.0050	2004-01-15 09.05		
~~mpb 114~~	0.0005	2004-01-15 09.05		
~~lfb 0.1 113~~	0.0905	2004-01-15 09.05		
~~lfb 0.04 113~~	0.0356	2004-01-15 09.05		
~~352684~~	0.0224	2004-01-15 09.05		
~~352683 mpk1~~	0.0953	2004-01-15 09.05		
~~352682 mpk2~~	0.0956	2004-01-15 09.05		
CNicv/ccv1	0.0934	2004-01-15 09.13		
CNicb/ccb1	<0.0000	2004-01-15 09.13		
~~352680~~	0.0011	2004-01-15 09.13		
mpb 114	0.0040	2004-01-15 09.13		
lfb 0.1 114	0.0985	2004-01-15 09.13		
352794	0.0043	2004-01-15 09.13		
352737	0.0165	2004-01-15 09.13		
352695 amen	0.0314	2004-01-15 09.13		
CNicv/ccv	0.0938	2004-01-15 09.21		
CNicb/ccb	<0.0000	2004-01-15 09.21		
352695 4 dup	0.0517	2004-01-15 09.21		
~~wa4 mdl1~~	0.0060	2004-01-15 09.21		
~~wa4 mdl2~~	0.0050	2004-01-15 09.21		
~~wa4 mdl3~~	0.0053	2004-01-15 09.21		
~~wa4 mdl4~~	0.0067	2004-01-15 09.21		
~~wa4 mdl5~~	0.0051	2004-01-15 09.21		
~~wa4 mdl6~~	0.0050	2004-01-15 09.21		
~~mdl wa4 7~~	0.0057	2004-01-15 09.21		
~~mpb wa4~~	0.0002	2004-01-15 09.21		
~~lfb 0.04 wa4~~	0.0991	2004-01-15 09.21		
CNicv/ccv 2	0.0949	2004-01-15 09.26		
CNicb/ccb 2	0.0007	2004-01-15 09.26		
~~Lfb 0.04 wa4~~	0.0442	2004-01-15 09.26		
CNicv/ccv	0.1049	2004-01-15 09.28		
CNicb/ccb	0.0011	2004-01-15 09.28		
~~352684~~ [redacted]	<0.19975	2004-01-15 09.33	1+99.0	1+1.0
CNicv/ccv	0.1017	2004-01-15 09.35		
CNicb/ccb	<0.0000	2004-01-15 09.35		
CNicv/ccv	0.0951	2004-01-15 09.53		
CNicb/ccb	<0.0000	2004-01-15 09.53		
0.2 mg/L	0.18856	2004-01-15 10.10		1+1.0
CNicv/ccv	0.0995	2004-01-15 10.12		
CNicb/ccb	0.0007	2004-01-15 10.12		
2 mg/L	1.82987	2004-01-15 10.16		1+19.0
CNicv/ccv	0.1037	2004-01-15 10.18		
CNicb/ccb	0.0005	2004-01-15 10.18		
mdl total mid: 6	0.0045	2004-01-15 10.27		
352682 free	<0.0000	2004-01-15 10.27		

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Approved By: D 9-10-09 QA Officer
Approved By: Heather L. Brady Area Supervisor

Attachment 23.4
Instrument Logbook Example

TriMatrix Laboratories, Inc.

Instrument Number 298 Run Logbook

Date	Analyst	Method Name or Number	Concentration of Calibration Standards Used							Units	Client Names and Sample Numbers
			No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7		
10-2-03	JWB	Cr+6	0	0.001	0.0025	0.005	0.01	0.025		mg/L	QC .01, .02 - E tech EG .10
			Calibration Requirements		≥0.995		Calibration Results		0.999621		
10-3-03	JWB	CN⁻	0	.005	.01	.02	.05	.10	.20	mg/L	344458-461, 533, 543, 344535, 344649-650
			Calibration Requirements		≥0.995		Calibration Results		0.999673		344534, 537, 831, 833, 834, 538, 830, 835, 836 344840, 841, 834, 542, 544, 815, 837
10-6-03	JWB	CN	0	.005	.01	.02	.05	.10	.20	mg/L	344991 345003, 004
			Calibration Requirements		≥0.995		Calibration Results		0.999946		e.tech 344992 - 998, 345000 - 007
		Cl	0	1	5	10	20	60	100	mg/L	344583 - 586, 687 - 695, 669 - 671
			Calibration Requirements		≥0.995		Calibration Results		1.0000		344283 - 303
		SO4	0	5	10	15	20/25	30	40	mg/L	↓ ↓
			Calibration Requirements		≥0.995		Calibration Results		1.0000		
10-7-03	JWB	CN⁻	0	.005	.01	.02	.05	.10	.20	mg/L	344958, 985, 953, 955, 954, 545, 546
			Calibration Requirements		≥0.995		Calibration Results		0.999914		345116 344955 - 960 344954, 957, 948, 571, 947, 345078
		Cl	0	1	5	10	20	60	100	mg/L	344813
			Calibration Requirements		≥0.995		Calibration Results		1.0000		

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Approved By: SOA 9-10-09 QA Officer
Approved By: Heather L. Brady Area Supervisor

Attachment 23.5
Batch Detail Report Example

TriMatrix Laboratories, Inc. **PREPARATION BATCH** 0711704 Page 1 of 2 Printed: 10/18/2007 3:06:03PM

Inorganic - Wet Chemistry, Waste Water, Method-Specific Preparation
(No Surrogate)
Batch Comments: (none)

Work Order	Analysis	Work Order	Analysis	Work Order	Analysis
0709675	Cyanide, Total 4500-CN E	0710014	Cyanide, Total 4500-CN E	0710045	Cyanide, Total 4500-CN E
0710058	Cyanide, Total 4500-CN E	0710059	Cyanide, Total 4500-CN E	0710085	Cyanide, Total 4500-CN E
0710075	Cyanide, Total 4500-CN E	0710129	Cyanide, Total 4500-CN E	0710186	Cyanide, Total 4500-CN E
0710218	Cyanide, Total 4500-CN E	0710248	Cyanide, Total 4500-CN E	0710261	Cyanide, Total 4500-CN E
0710265	Cyanide, Total 4500-CN E	0710288	Cyanide, Total 4500-CN E	0710321	Cyanide, Total 4500-CN E
0710349	Cyanide, Total 4500-CN E				

Lab Number	Container	Prepared	By	Initial (mL)	Final (mL)	uL Surrogate	Source ID	Spike ID	uL Spike	Client / QC Type	Extraction Comments
0711704-BLK1		Oct-03-07 07:44	VAS	50	50					BLANK	
0711704-BS1		Oct-03-07 07:44	VAS	50	50			7100016	50	LCS	
0711704-BS2		Oct-03-07 07:44	VAS	50	50			7100016	35	LCS	
0709675-01	B	Oct-03-07 07:44	VAS	50	50					[redacted]	
0710014-01	B	Oct-03-07 07:44	VAS	50	50					[redacted]	
0710014-03	B	Oct-03-07 07:44	VAS	50	50					[redacted]	
0710014-05	B	Oct-03-07 07:44	VAS	50	50					[redacted]	
0710014-07	B	Oct-03-07 07:44	VAS	50	50					[redacted]	
0710045-01	B	Oct-03-07 07:44	VAS	50	50					[redacted]	0 9 07
0711704-BLK2		Oct-08-07 07:44	VAS	50	50					BLANK	
0711704-BS3		Oct-08-07 07:44	VAS	50	50			7100016	50	LCS	
0711704-BS4		Oct-08-07 07:44	VAS	50	50			7100016	20	LCS	
0711704-MS1		Oct-08-07 07:44	VAS	50	50		0710075-06	7100016	50	MATRIX SPIKE	
0711704-MSD1		Oct-08-07 07:44	VAS	50	50		0710075-06	7100016	50	MATRIX SPIKE DUP	
0710058-01	D	Oct-08-07 07:44	VAS	50	50					[redacted]	
0710069-01	D	Oct-08-07 07:44	VAS	50	50					[redacted]	
0710085-02	B	Oct-08-07 07:44	VAS	50	50					[redacted]	
0710075-06	J	Oct-08-07 07:44	VAS	50	50					[redacted]	4 17 07
0710129-04	H	Oct-08-07 07:44	VAS	50	50					[redacted]	4 13 07

Comments

Analyst Initials

tch_TriMatrix.rpt

TriMatrix Laboratories, Inc. **PREPARATION BATCH** 0711704 Page 2 of 2 Printed: 10/18/2007 3:06:03PM

Inorganic - Wet Chemistry, Waste Water, Method-Specific Preparation
(No Surrogate)
Batch Comments: (none)

Lab Number	Container	Prepared	By	Initial (mL)	Final (mL)	uL Surrogate	Source ID	Spike ID	uL Spike	Client / QC Type	Extraction Comments
0711704-BLK3		Oct-15-07 07:45	LMA	50	50					BLANK	
0711704-BS5		Oct-15-07 07:45	LMA	50	50			7100016	50	LCS	
0711704-BS6		Oct-15-07 07:45	LMA	50	50			7100016	20	LCS	
0710186-02	A	Oct-15-07 07:45	LMA	50	50					[redacted]	
0710218-01	A	Oct-15-07 07:45	LMA	50	50					[redacted]	4 12 07
0710245-01	D	Oct-15-07 07:45	LMA	50	50					[redacted]	
0710261-01	A	Oct-15-07 07:45	LMA	50	50					[redacted]	
0710265-01	D	Oct-15-07 07:45	LMA	50	50					[redacted]	
0710266-01	D	Oct-15-07 07:45	LMA	50	50					[redacted]	
0710321-01	A	Oct-15-07 07:45	LMA	50	50					[redacted]	
0711704-BLK4		Oct-16-07 07:00	LMA	50	50					BLANK	
0711704-BS7		Oct-16-07 07:00	LMA	50	50			7100401	50	LCS	
0711704-BS8		Oct-16-07 07:00	LMA	50	50			7100401	20	LCS	
0710349-01	A	Oct-16-07 07:00	LMA	50	50					[redacted]	4 12 07

Comments

Analyst Initials

tch_TriMatrix.rpt

UNCONTROLLED COPY

Approved By: 9-10-09 **QA Officer**

Approved By: Heather L. Brady **Area Supervisor**

TriMatrix Laboratories, Inc.

UNCONTROLLED COPY

STANDARD OPERATING PROCEDURE

Block Digestion of Aqueous Samples and Extracts for Total/Dissolved Metals by ICPMS

SW-846 Method 3020A

APPROVALS:

Area Supervisor: Marge A. Scott — Date: 01-14-09

QA Officer: Tom C. Boocher — Date: 1-8-09

Operations Manager: Jeff P. Glaser — Date: 1/15/09

Procedure Number: GR-01-148
Revision Number: 0.3

Date Initiated: 12/3/01
Effective Date: 1/20/09

Date Revised: 1/7/09
Pages Revised: All

By: Marge A. Scott

Total Number of Pages: 13

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

1.0 SCOPE AND APPLICATION

1.1 This procedure outlines total metals digestion in water and leachate samples with the exception of silica-based matrices. Also outlined is the preparation of aqueous samples for dissolved metals analysis. A block digestion system is used when digestion is required.

1.2 Samples that have been filtered and acidified for dissolved metals analysis do not need the acid digestion unless otherwise specified.

1.2 The digestion is for analysis by inductively coupled plasma/mass spectrum (ICP/MS).

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 1, July 1992, Method 3020A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy"

3.0 SUMMARY OF PROCEDURE

3.1 A representative sample aliquot is refluxed in nitric acid until the solution is light in color or the color remains stable. The digestate is then diluted to a predetermined volume for analysis.

3.2 Deviation from the referenced method involves sample volume reduction from 100 to 25 mL, with nitric acid additions adjusted in direct proportion to the volume reduced.

4.0 PARAMETER OR COMPOUND LIST

4.1 Refer to Attachment 20.1.

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal*, latest revision

5.2 TriMatrix SOP GR-16-103, Glassware Cleaning and Preparation for the Wet Chemistry and Metals Laboratories, latest revision

5.3 TriMatrix SOP GR-10-125, *Method Detection Limit (MDL)*, latest revision

5.4 TriMatrix SOP GR-10-111, *Fixed and Adjustable Mechanical Pipette and Bottle Top Dispenser Calibration Verification*, latest revision

5.5 TriMatrix SOP GR-10-113, *Laboratory Balance Calibration and Verification*, latest revision

5.6 TriMatrix SOP GR-10-106, Inorganic and Metals Laboratories Corrective Actions, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Samples must be at room temperature before a digestion aliquot can be taken to assure measurement accuracy.

7.0 SAFETY PRECAUTIONS

7.1 Refer to the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan for routine precautions.

7.2 Gloves, approved safety glasses and laboratory coats must be worn at all times when handling acids and when performing this procedure. An impervious plastic apron is also required when handling significant volumes of acid.

7.3 Concentrated nitric acid fumes burn, discolor the skin and give off poisonous gases. Fume hoods must be used during handling and when performing this procedure.

7.4 Rinse all micropipette tips and beakers before cleaning or disposal. Do not dispose of acid rinses before neutralizing.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND MATERIALS

8.1 Samples must be acidified at the time of collection to a pH of <2 with nitric acid. If the pH is not <2 when received by the laboratory, lower to <2 during sample receipt using 1:1 nitric acid/water. The maximum allowable acid volumes that may be added to a sample (including initial volume) are:

Container Size (mL)	Acid Volume (mL)
125	1.2
250	2.6
500	5.0
1000	10

Note: Sample preservation must occur in the original container to prevent analyte loss from plating out on the container wall. It is <u>not</u> permissible to remove and acidify a sample aliquot.

8.2 If pH adjustment is necessary when received at the laboratory, a minimum of 24 hours must elapse before the sample may be digested.

8.3 Consult the project chemist for instructions if the pH cannot be adjusted to <2 using the maximum acid volume. Samples digested and analyzed without proper pH preservation, results must be narrated as such.

8.4 Samples must be collected in plastic. Do not allow acidified sample to come into contact with metal to prevent contaminants dissolving into the sample.

8.5 To ensure sufficient sample volume for quality control and/or redigestion, collect at least 500 mL of unfiltered liquid. Smaller volumes may result in elevated reporting limits.

8.6 Samples collected for dissolved metals analysis must be filtered and the filtrate acidified at the time of collection. For some sample determinations of dissolved elements, the filtered/acidified filtrate may require digestion.

8.7 Appropriately acid-preserved samples may be held for up to 180 days prior to digestion. Refrigeration is not required for samples or digestates.

9.0 INSTRUMENTATION, APPARATUS AND MATERIALS

9.1 Micropipetter – capable of delivering 25 and 100 uL

9.2 Block digester for metals digestion – Environmental Express HotBlock™

9.3 Digestion cups, polypropylene, certified precleaned – Environmental Express SC499 or SC500

9.4 Ribbed watch glasses – Environmental Express SC505

9.5 Filtermate (digestate filtration) – Environmental Express SC0501

Note: If digestates are filtered after digestion, all associated quality control must be filtered as well.

9.6 Nonribbed watch glasses – SCP Science 010-500-081

9.7 Filtration units, vacuum pump, for dissolved sample filtering in the field

Note: Each lot of filtration units received must be verified by running a dissolved blank and a dissolved blank spike. Results must be uploaded to Element™.

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Verify and document micropipette calibration daily.

10.2 Clean block digestion units and counters daily and/or when spills occur.

11.0 CHEMICALS AND REAGENTS

11.1 Laboratory distilled, deionized water (ASTM Type II) - designated in this procedure as metals-free water

11.2 Concentrated nitric acid (HNO_3), trace metal grade

12.0 STANDARDS PREPARATION

12.1 Multi-element ICPMS certified spiking standards are listed in Attachment 20.1.

13.0 ANALYTICAL PROCEDURE

13.1 Prepare samples that have been filtered through a 0.45 µm filter and acidified in the field as follows:

13.1.1 If a filtered/acidified sample exhibits a strong organic odor, digest before analysis.

Note: Do not directly smell any sample.

13.1.2 If a filtered/acidified sample exhibits significant color, digest before analysis.

13.1.3 If a filtered/acidified sample has a turbidity greater than 1 NTU, digest before analysis.

13.1.4 If a filtered/acidified sample forms a precipitate at preservation, during transit to the laboratory or in storage, digest before analysis.

13.2 To perform the digestion, mix samples by shaking vigorously to achieve homogeneity. After mixing, measure 25.0 mL of sample (or an appropriate dilution) into a polypropylene digestion cup using the cup graduations. For samples requiring matrix spikes, shake again before subsequent 25.0 mL transfers.

Note: Each digestion cup lot needs verified for acceptable accuracy at 25 mL by weighing out 25 mL of metals-free water on the analytical balance. Then, calculate the average volume measured and uncertainty.

13.3 Add 0.75 mL concentrated HNO_3, cover each cup with a ribbed watchglass and reflux in the block digester at 90 - 95° C. Adjust the block digester temperature to 85° C before refluxing to account for the watchglass, which adds ten degrees. Refer to the HotBlock™ operating manual for temperature adjustment and principles of operation. Evaporate to near dryness which is approximately 1.25 mL but don't let any digestion go completely dry.

13.4 After reducing to about 1.25 mL, remove from the block digester and cool to room temperature.

13.5 Add 0.75 mL concentrated HNO_3, cover with a nonribbed watchglass and gently reflux for 30 minutes. Repeat with additional acid as necessary, until the digestate is light in color or does not change in appearance with continued refluxing.

13.6 When digestion is complete, evaporate to 0.75 mL using a ribbed watchglass. Do not let any part of the digestion cup bottom evaporate to dryness. If a digestate evaporates to dryness, it must be repeated.

13.7 Remove from the block digester and add 2.5 mL metals-free water. Mix and continue warming for 15 minutes.

13.8 Remove from the block digester and cool to room temperature.

13.9 After cooling, dilute to 25.0 mL with metals-free water, cap tightly and shake vigorously.

14.0 DATA REPORTING AND DELIVERABLES

14.1 All samples that require digestion and must be input as pretreated to the Laboratory Information Management System (Element™).

14.2 Each sample batch of up to 20 samples referencing the same digestion method is given an Element™ batch number.

14.2 The batch number is used to segregate digestion batches for analysis. The batch number is also used by Element™ to associate quality control with associated sample results.

15.0 QUALITY ASSURANCE

15.1 A Digestion Blank (BLK) must be carried through the entire procedure to monitor for contamination with each digestion batch of up to 20 samples. The BLK is prepared by measuring 25 mL of metals-free water or appropriate leachate extraction fluid into a digestion cup for digestion.

Note: A dissolved metals blank is metals-free water that is matrix-matched to instrument standards at the instrument.

15.2 A digestion Blank Spike (BS) must be carried through the entire procedure to monitor recovery for each digestion batch.

15.2.1 The digestion blank spike is prepared by measuring 25.0 mL of metals-free water or appropriate leachate extraction fluid into a digestion cup and spiking with 25 µL each of two 50 mg/L mixed metals solutions (refer to Attachment 20.1).

15.2.1.1 HP2079-1-1L, stock solution A (100 mg/L) is diluted to 50 mg/L and designated QCA.

15.2.1.2 HP2079-2-1L, stock solution B (100 mg/L), is diluted to 50 mg/L and designated QCB.

15.2.2 A dissolved metals blank spike is prepared in metals-free water, spiked as above then matrix-matched to the instrument standards.

15.3 Perform matrix spike/matrix spike duplicates (MS/MSD) for each digestion batch of up to 20 samples for each matrix type.

15.3.1 The digestion matrix spike is prepared by measuring 25.0 mL of sample into a digestion cup and spiking with 25 µL each of two 50 mg/L mixed metals solutions (refer to Attachment 20.1).

15.3.1.1 HP2079-1-1L, stock solution A (100 mg/L) is diluted to 50 mg/L and designated QCA.

15.3.1.2 HP2079-2-1L, stock solution B (100 mg/L), is diluted to 50 mg/L and designated QCB.

15.3.2 A dissolved metals matrix spike is prepared in filtered/acidified sample, matrix-matched to the instrument standards and spiked as above.

15.4 If a digestate evaporates to dryness, some metals will be volatized. If any portion of a digestion cup bottom goes dry, discard the digestate and redigest in another batch.

15.5 Digestates must not boil during evaporation. If a digestate begins boiling, immediately remove from the block digester and reduce the temperature setting. Excessive boiling will cause analyte loss. If a digestate boils during evaporation, it must be discarded and the sample redigested in another batch.

15.6 Standard solutions must be used within the predetermined expiration date. If a standard or solution has expired, remove it from the laboratory for proper disposal and obtain or prepare another.

15.7 Quality control acceptance limits are listed in Element™.

15.8 Address unacceptable quality control and perform corrective action in accordance with TriMatrix SOP GR-10-106.

16.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

16.1 Before processing actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC).

16.1.1 To perform an IDC, prepare four blank spikes by spiking 25 mL of metals-free water with 25 µL of 50 mg/L spiking standard.

16.1.2 Digest as samples, following every step in the procedure and analyze.

16.1.3 Input results to the IDC spreadsheet located on the laboratory intranet library to calculate average percent recovery and relative standard deviation.

16.1.4 Average recovery must fall within the blank spike control limits in Element™. Relative standard deviation must not be higher than 20%.

16.1.5 If any criterion is not met, locate and correct the source of the problem and repeat the study successfully.

16.1.6 Repeated failure however, will confirm a general problem with the procedure and/or techniques used. If multiple failures occur, correct the procedure and/or technique used, revise the procedure and repeat the study successfully.

16.1.7 Samples may not be processed by any analyst until an IDC study has been successfully completed.

16.1.8 Submit a copy of the successful IDC spreadsheet to the Quality Assurance department for training documentation.

16.2 Annually, a Continuing Demonstration of Capability (CDC) is required by each analyst by any of the following approaches:

16.2.1 By repeating the IDC study.

16.2.2 By inputting the last four results from a method detection limit (MDL) study to the IDC spreadsheet if prepared exclusively by the analyst.

16.2.3 By inputting four consecutive blank spike results obtained during the course of routine sample analysis to the IDC spreadsheet if prepared exclusively by the analyst.

16.2.4 By obtaining a passing result on a blind performance testing study if prepared exclusively by the analyst.

16.3 A method detection limit (MDL) study is required annually in accordance with TriMatrix SOP GR-10-125.

17.0 POLLUTION PREVENTION

17.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

17.2 Never dispose of laboratory chemicals without first referencing appropriate written instructions of disposal for that particular material.

17.3 Conserve the use of chemicals where applicable

17.4 Comply with all environmental laws associated with chemicals in the laboratory.

18.0 WASTE MANAGEMENT

18.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals.

18.2 To minimize the environmental impact and costs associated with the disposal of chemicals, order and use only the minimum amount of material required.

18.3 Follow all instructions in TriMatrix SOP GR-15-102, *Laboratory Waste Disposal*, for laboratory waste disposal requirements.

19.0 REFERENCES

19.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 1, July 1992, Method 3020A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy"

20.0 ATTACHMENTS

20.1 Analyte List

20.2 Example Preparation Batch Report

20.3 Example Environmental Express Certificate of Analysis, Solution A

20.4 Example Environmental Express Certificate of Analysis, Solution B

Attachment 20.1
Analyte List

Element	Environmental Express Stock Solution
Aluminum	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Antimony	HP2079-1-1L (QCB) 100 mg/L diluted to 50 mg/L
Arsenic	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Barium	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Beryllium	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Boron	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Cadmium	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Chromium	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Cobalt	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Copper	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Lead	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Manganese	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Nickel	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Selenium	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Silver	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Strontium	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Thallium	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Tin	HP2079-1-1L (QCB) 100 mg/L diluted to 50 mg/L
Vanadium	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L
Zinc	HP2079-1-1L (QCA) 100 mg/L diluted to 50 mg/L

Approved By: RM 1-8-09
QA Officer

Approved By: MAS 01-14-09
Area Supervisor

Attachment 20.2
Example Preparation Batch Report

TriMatrix Laboratories, Inc. **PREPARATION BATCH** 0808883 Page 1 of 1 Printed: 8/11/2008 2:04:12PM

Metals, Water, 3020A Digestion

Batch comments:
MAS 07/30/08 7:35AM-3:30PM
INST#217 @95C#195
HOTBLOCK VESSEL LOT#A801LP001

Lab Number	Container	Prepared	By	Initial (mL)	Final (mL)	Client Source ID	Client Spike ID	Client uL Spike	Comments
0807506-01	O	Jul-30-08 07:35	MAS	25	125	[redacted]			
Ag Total 6020	*As Total 6020*	*B Total 6020*	*Ba Total 6020*	*Be Total 6020*	*Cd Total 6020*	*Co Total 6020*	*Cr Total 6020*		
Cu Total 6020	*Ni Total 6020*	*Pb Total 6020*	*Sb Total 6020*	*Se Total 6020*	*Tl Total 6020*	*V Total 6020*	*Zn Total 6020*		
0807506-02	E	Jul-30-08 07:35	MAS	25	125	[redacted]			
Ag Total 6020	*As Total 6020*	*B Total 6020*	*Ba Total 6020*	*Be Total 6020*	*Cd Total 6020*	*Co Total 6020*	*Cr Total 6020*		
Cu Total 6020	*Ni Total 6020*	*Pb Total 6020*	*Sb Total 6020*	*Se Total 6020*	*Tl Total 6020*	*V Total 6020*	*Zn Total 6020*		
0808883-BLK1		Jul-30-08 07:35	MAS	25	125				
0808883-BS1		Jul-30-08 07:35	MAS	25	125		8070952	25	
0808883-MS1		Jul-30-08 07:35	MAS	25	125	0807506-02	8070952	25	
0808883-MSD1		Jul-30-08 07:35	MAS	25	125	0807506-02	8070952	25	
0808883-PS1		Aug-04-08 09:40	DSC	2	10	0807506-02	7110622	50	

Comments:	Analyst Initials:

bch_TM_byAnalysis.rpt

Approved By: QA 1-8-09 **QA Officer**

Approved By: MAS 01-14-09 **Area Supervisor**

Attachment 20.3
Example Environmental Express Certificate of Analysis, Solution A

Me 14.62.4
A 505048

ENVIRONMENTAL EXPRESS

Certificate of Analysis

HP2079-1-1L
SOLUTION A
Lot # 511212

Source	Source Purity	Matrix	Standard Concentration
High Purity Metals, Salts, or Oxides	99.99+%	HNO_3, 3.5%	mg/L ± 0.5% See elements listed on reverse

This spectrometric standard solution has been prepared from high-purity reference materials. Subboiled high-purity acid has been used to place the materials in solution and to stabilize the standard. The matrix is as noted above in 18 megaohm deionized water. The reference materials have been assayed by optical emission spectrometry and atomic absorption spectrometry.

The standard has been prepared gravimetrically by weighing the reference material to 5 significant figures. Volumetric glassware has been calibrated gravimetrically to 5 significant figures.

The Standard Concentration has been certified by spectrometric analysis against an independent source which is directly traceable to National Institute of Standards and Technology, Standard Reference Material No. 3100 series, and checked by ICP prior to shipping.

This solution is valid for a period of one year from the shipping date provided the solution is kept tightly capped and stored under normal laboratory conditions.

Theodore C. Rains, Ph.D.
Laboratory Director

Exp. Date MAY 06
MSDS ATTACHED

490 Wando Park Blvd.
Mt. Pleasant, South Carolina 29464
Phone: 1.843.881.6560
Toll Free: 1.800.343.5319
FAX: 1.843.881.3964
www.environmentalexpress.com

Approved By: 1-8-09 QA Officer
Approved By: MAS 01-14-09 Area Supervisor

Attachment 20.4
Example Environmental Express Certificate of Analysis, Solution B

ENVIRONMENTAL EXPRESS

Certificate of Analysis

HP2079-1-1L
Solution B
Lot # 631157

6110557
DSL
11-15-06
EXP. 12-01-07

Source	Source Purity	Matrix	Standard Concentration
High Purity Metals, Salts or Oxides	99.98+%	HNO_3, 2% + Tr HF	100 mg/L ± 0.5% Antimony Silicon from $(NH_4)_2SiF_6$ Titanium Molybdenum Tin

This spectrometric standard solution has been prepared from high-purity reference materials. Sub-boiling distilled high-purity acid has been used to place the materials in solution and to stabilize the standard. The matrix is as noted above in 18 megaohm deionized water. The reference materials have been assayed by inductively coupled plasma optical emission spectrometry (ICP-OES).

The standard has been prepared gravimetrically by weighing the reference material to 5 significant figures. Volumetric glassware has been calibrated gravimetrically to 5 significant figures. The standard concentration has been verified by ICP-OES against an independent source which is traceable to National Institute of Standards and Technology, Standard Reference Material No. 3100 series.

This standard is valid for one year from the shipping date provided the solution is kept tightly capped and stored under normal laboratory conditions.

Theodore C. Rains, Ph.D.
Laboratory Director

Exp Date: DEC '07
MSDS ATTACHED

490 Wando Park Blvd.
Mt. Pleasant, South Carolina 29464
Phone: 1.843.881.6560
Toll Free: 1.800.343.5319
FAX: 1.843.881.3964
www.environmentalexpress.com

Approved By: DB 1-8-09 QA Officer
Approved By: MAS 01-14-09 Area Supervisor

TriMatrix Laboratories, Inc.

UNCONTROLLED COPY

STANDARD OPERATING PROCEDURE

Block Digestion of Total Metals in Water for ICP

EPA Method 200.7
SW-846 Method 3010A

APPROVALS:

Area Supervisor: Marge A Scott — Date: 01/14/09
Marge A. Scott

QA Officer: [signature] — Date: 1-8-09
Tom C. Boocher

Operations Manager: Jeff Glaser — Date: 1/15/09
Jeff P. Glaser

Procedure Number: GR-01-147
Revision Number: 0.4

Date Initiated: 7/15/03
Effective Date: 1/20/09

Date Revised: 1/7/09
Pages Revised: All

By: Marge A. Scott

Total Number of Pages: 16

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

1.0 SCOPE AND APPLICATION

1.1 Water, wastewater and leachate samples are prepared for total metals analysis by block digestion.

1.2 Silica-based matrices are not digested using this procedure.

1.3 Digestates are prepared for analysis by inductively coupled plasma spectrometry (ICP).

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846,* 3rd Edition, Final Update III, Revision 1, July 1992, Method 3010A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy"

2.1.1 This procedure describes the use of a 50 mL non-constricted block digestion cup as a deviation from method 3010A, which specifies the use of a Griffin beaker.

2.1.2 This procedure describes the use of 25 mL as a deviation from method 3010A, which specifies a 100 mL sample aliquot for digestion.

2.1.3 This procedure describes the use of 5 mL of nitric acid for the first reflux as a deviation from method 3010A which specifies 3 mL. Acid ratios are maintained and 1.25 mL is used for 25 mL instead of 5 mL for 100 mL.

2.2 *Code of Federal Regulations*, Title 40, Appendix C to Part 136, February 1, 2002, Method 200.7, "Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes"

2.2.1 This procedure describes the use of a 50 mL block non-constricted digestion cup as a deviation from method 200.7, which specifies the use of a Griffin beaker.

3.0 SUMMARY OF PROCEDURE

3.1 Samples are prepared as follows:

3.1.1 A 25.0 mL aliquot of well-mixed, homogeneous aqueous sample is accurately measured into a digestion cup.

3.1.2 Analytes are solubilized by evaporating the sample to low volume after adding nitric acid while gently refluxing. Additional portions of nitric acid are added with further refluxing until the digestate is light in color or has color-stabilized.

3.1.3 The digestate is then gently refluxed with 1:1 (v/v) hydrochloric acid to dissolve any precipitate.

3.1.4 After digestion is complete and cool, the volume is adjusted with laboratory reagent water to 25.0 mL.

4.0 PARAMETER OR COMPOUND LIST

4.1 This procedure includes digestion for the following elements:

Aluminum	Chromium	Selenium	Calcium	Potassium
Antimony	Cobalt	Silver	Iron	Silicon
Arsenic	Copper	Strontium	Lithium	Sodium
Barium	Lead	Thallium	Magnesium	Sulfur
Beryllium	Manganese	Tin	Phosphorus	Titanium
Boron	Molybdenum	Vanadium		
Cadmium	Nickel	Zinc		

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal*, latest revision

5.2 TriMatrix SOP GR-01-100, *Inductively Coupled Plasma Atomic Emission Spectrometry using Perkin Elmer Optima 3000/3300DV*, latest revision

5.3 TriMatrix SOP GR-01-145, *Inductively Coupled Plasma Atomic Emission Spectrometry using Perkin Elmer Optima 3000/3300DV*, latest revision

5.4 TriMatrix SOP GR-10-106, *Inorganic and Metals Laboratories Corrective Actions*, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Refer to TriMatrix SOP GR-01-145 for a list of interferences and associated corrective actions when digesting for ICP analysis.

7.0 SAFETY PRECAUTIONS

7.1 Comply with all instructions for health and safety as outlined in the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan.

7.2 Concentrated acids are used in standard and sample preparations. Wear disposable gloves, laboratory coats and approved safety glasses at all times when digesting samples and/or working in the laboratory.

7.3 Refer to the Material Safety Data Sheet (MSDS) library for specific information on any chemical used in the laboratory.

7.4 Check fume hoods to be sure each is functioning properly. All digestions must be done in a fume hood. If the hood is not working properly, immediately contact the area supervisor. Under no circumstances is any block digestion to be performed if the exhaust hood is not function properly.

7.5 Many chemicals and elements used in this procedure are toxic. Minimize exposure by appropriate use of the personal protective equipment provided.

7.6 No food or drink is allowed in the digestion laboratory at any time, including gum.

7.7 Wash hands before starting work. Substances on the skin may interfere with metals analysis. Wash hands after finishing work. Chemical residuals can be injested and/or carried out of the laboratory if not removed.

7.8 Before leaving the digestion laboratory, remove disposable gloves and laboratory coat. Chemical and/or acid residue transport outside the digestions laboratory needs to be kept to a minimum.

7.9 Rinse all micropipette tips and beakers before disposal or cleaning.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND MATERIALS

8.1 Samples collected for digestion and analysis by ICP can be preserved in the field or upon receipt by the laboratory. If the pH is not <2 when received by the laboratory, lower to <2 during the sample receipt process using 1:1 nitric acid/water. The maximum volumes of acid added to a sample (including initial volume) are:

Container Size	Acid Volume (mL)
125	1.2
250	2.6
500	5.0
1000	10.0

8.2 If a pH adjustment is necessary, a minimum of 24 hours must elapse before the sample digestion process may begin.

NOTE: Sample preservation must occur in the original container to prevent the loss of any analytes adsorbed to the container wall. It is not permissible to remove and acidify a sample aliquot.

NOTE: If the sample must be analyzed within 24 hours of collection, the sample must be preserved immediately during collection.

NOTE: If boron is an analyte of interest the sample must be preserved immediately during collection.

NOTE: Samples collected for pre-treatment and analysis by method 6010 must be preserved immediately during collection.

8.3 Consult the project chemist for instruction if the pH cannot be adjusted to <2 using the specified maximum amount of acid. Samples prepared and analyzed without proper pH preservation, results must be narrated as such.

8.4 Samples may be collected in glass or plastic. If Boron is to be analyzed, use only plastic containers. Do not allow acidified sample to come into contact with metal to prevent contaminants dissolving into the sample.

8.5 To ensure sufficient sample volume for quality control and/or redigestion, collect at least 150 mL of unfiltered liquid. Smaller volumes may result in elevated reporting limits.

8.6 For some determinations of dissolved elements, the filtered and preserved sample may require digestion. Filtered samples that form a precipitate at preservation, during transit to the laboratory or in storage must be digested before the analysis.

8.7 Properly acid-preserved samples can be held for up to 180 days prior to digestion. Refrigeration is not required for samples or digestates.

9.0 INSTRUMENTATION, APPARATUS AND MATERIALS

9.1 Micropipette, capable of delivering 125 µL

9.2 Block digestor for metals digestion, Environmental Express, HotBlock™, model SC154

9.3 Block digestion cups, certified pre-cleaned, catalog SC475, available from Environmental Express

9.4 Ribbed watchglasses, disposable, Environmental Express, catalog SC505

9.5 Filtermate, Environmental Express, catalog SC0501, for digestate filtration

9.6 Non-ribbed watchglasses, disposable, Environmental Express, SCP Science, catalog 010-500-081

9.7 Thermometers, NIST-traceable, digital, capable of reading to at least 100° C in 0.1° C increments.

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Verify and document the micropipette calibration daily.

10.2 Clean each block digestor and all counters daily. Clean up spills immediately.

11.0 CHEMICALS AND REAGENTS

11.1 Laboratory reagent water (ASTM Type II), milliQ water system

11.2 Nitric acid (HNO_3), concentrated, trace metal grade

11.3 Hydrochloric acid (HCl), concentrated, trace metal grade

11.3.1 Prepare a 1:1 (v/v) solution of HCl in water by measuring 50 mL of concentrated HCl into 50 mL of laboratory reagent water. Remember to perform the addition in a fume hood.

11.3.2 Expiration is six months from the date made.

12.0 STANDARDS PREPARATION

12.1 Multi-element ICP spiking solutions are purchased as commercially prepared solutions. Refer to Attachments 20.1 and 20.2 for ICP spiking solution examples.

13.0 ANALYTICAL PROCEDURE

13.1 Fill one block digestion cup with laboratory reagent water and place in a random hole of the block digestor. Cover with a watchglass that has a hole in the center and insert the digital thermometer through the hole. Using the thermometer and not the block digestor read-out, adjust the block temperature to 90 - 95° C.

13.2 Mix samples by vigorously shaking to achieve homogeneity. Immediately after shaking, measure 25.0 mL (or an appropriately smaller volume) into a block digestion cup. For samples requiring matrix spikes, shake vigorously before each 25.0 mL aliquot is removed.

13.3 Measure 0.75 mL of concentrated HNO_3 into each sample cup then cover with a ribbed watchglass.

13.4 After the block equilibrates to 90 - 95° C, place all samples in the block and cover with a ribbed watchglass. Evaporate to near dryness, which is approximately 1.25 mL. If necessary, measure 1.25 mL into an empty digestion cup for comparison. If any digestion goes to dryness, discard and re-prepare with another sample aliquot.

13.5 After evaporating to near dryness, cool by removing briefly from the block then add 1.25 mL of concentrated HNO_3. Cover with a non-ribbed watchglass then return to the block and gently reflux. Slight boiling should occur while refluxing but vigorous boiling must be avoided. Continue refluxing. If the digestate is not light in color after refluxing, cool and add another 0.75 mL HNO_3 then continue refluxing as before. Repeat 0.75 mL HNO_3 additions and refluxing until the digestate is light in color or does not change with continued refluxing.

13.6 When the digestion is complete, change to a ribbed watchglass and evaporate to approximately 0.75 mL. Be careful not to let any digestion go to dryness, else it will need discarded and re-prepared.

13.7 After evaporation to 0.75 mL, remove from the block to cool then measure 2.5 mL of 1:1 HCl into each digestate. Return to the block and gently reflux for an additional 15 minutes.

13.8 After refluxing with HCl, remove from the block and cool to room temperature.

13.9 When cool, dilute to 25.0 mL with laboratory reagent water then cap and shake vigorously. At this point, digestates are ready for analysis.

14.0 DATA REPORTING AND DELIVERABLES

14.1 Work orders are printed out by the Laboratory Information Management System (Element™) indicating which samples need digestion.

14.1.1 Initial and date any hand-written information on the work order report.

14.1.2 Organize and archive all work order forms in accordance with the TriMatrix quality assurance manual.

14.2 Completion of each sample with all quality control is entered back into Element™ and a preparation batch report is printed.

14.2.1 Enter all information associated with the digestion before printing.

14.2.2 The preparation batch report accompanies the sample digestion batch to the instrumental laboratory.

14.2.3 Initial and date any hand-written information on the preparation batch report.

14.2.4 Organize and archive all preparation batch report forms in accordance with the TriMatrix quality assurance manual.

14.3 Maintain the use of all standards and reagents in Element™ for traceability. Certificates of analysis are maintained on the laboratory intranet library for each standard and reagent used.

14.4 Analysts preparing digestion batches are responsible for correctly filling in, transferring and filing all associated paperwork. This is essential in providing the client with defensible data.

14.5 If internal chain-of-custody (COC) is required, it is very important that COC forms be filled in completely and correctly. Organize, transfer and/or archive COC forms in accordance with the TrMatrix quality control manual.

14.6 Fill in block digestor maintenance logbooks completely and correctly when maintenance is performed. Indicate blank areas in logbooks with a large "Z" that is dated and initialed.

14.7 Make corrections in any logbook or on any hardcopy with a single line over the mistake (not a writeover or scribble) then date and initial any new writing.

15.0 QUALITY ASSURANCE

15.1 At least one digestion blank (BLK) must be carried through the entire digestion to monitor contamination with each digestion batch of up to 20 samples. The blank is prepared by measuring 25.0 mL of laboratory reagent water or appropriate extraction fluid into a digestion cup and digesting as a sample.

15.2 At least one blank spike (BS) must be carried through the entire digestion to document recovery without matrix interference in each digestion batch of up to 20 samples. A blank spike is prepared by measuring 25.0 mL of laboratory reagent water or appropriate extraction fluid into a digestion cup, then spiking with 125 µL of solution SSW-1A and 125 µL of solution SSW/SSS-2A.

15.3 Prepare a matrix spike (MS) and matrix spike duplicate (MSD) for water samples, for each digestion batch of up to 20 samples.

15.4 Prepare a matrix spike (MS) and matrix spike duplicate (MSD) for leachates, for each digestion batch of up to 20 samples.

15.5 Prepare a matrix spike (MS) and matrix spike duplicate (MSD) for wastewater samples, for each digestion batch of up to 10 samples.

15.6 Prepare matrix spike and matrix spike duplicates by measuring a 25.0 mL sample aliquot into a digestion cup, then spiking with 125 µL of solution SSW-1A and 125 µL of solution SSW/SSS-2A.

15.7 Digestates must not boil during the evaporation step. If a digestate begins to boil during evaporation, immediately remove from the block and reduce the temperature. Some boiling will be evident during the reflux step. However, vigorous boiling during reflux will diminish the water-acid azeotrope and cause loss of analyte. If a digestate begin to boils vigorously during refluxing, immediately remove from the block and reduce the temperature. If boiling during evaporation or vigorous boiling during refluxing is not immediately addressed, discard and the re-prepare the sample and/or samples affected. Monitor the block temperature closely to minimize re-preparation.

15.8 Each commercially purchased spiking solution must be used within its expiration date. If a standard or solution has expired, remove it from the laboratory for proper disposal.

16.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

16.1 Before processing actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC). Analysts responsible for sample processing by this procedure must pass an IDC study first.

16.1.1 Initial Demonstration of Capability Study

16.1.1.1 Spike four 25.0 mL aliquots of laboratory reagent water as in a blank spike preparation. Digest the four spikes following every step in this procedure and obtain analysis results for the four blank spikes. Analysis of the spikes must also include every step in the analytical procedure. Enter all four results obtained into the IDC spreadsheet located on the laboratory intranet library to calculate average percent recovery and relative standard deviation. Average recovery must fall

within the blank spike control limits found in Element™. Relative standard deviation must be less than or equal to 20%.

16.1.1.2 Alternatively, the last four of seven results used in an MDL study may be used as the IDC, if the MDL study was run exclusively by the analyst. ONLY the last four results may be used.

16.1.1.3 If either criterion is not met, locate and correct the source of any problem and repeat the study to confirm the corrective action was successful. Repeated failure however, will confirm a general problem with the procedure or techniques used. If multiple failures occur, correct the procedure or techniques used, and repeat the study.

16.1.1.4 Samples may not be processed by any analyst until an IDC study has been successfully completed. Give copies of successful IDC study spreadsheets and raw data to the quality assurance department for training documentation.

16.1.2 Continuing Demonstration of Capability Study

16.1.2.1 Annually, a Continuing Demonstration of Capability (CDC) study is required by each analyst.

16.1.2.2 A CDC may be accomplished by repeating the IDC study, by using the last four results from an MDL study, or by using four consecutive and exclusively run blank spike results obtained from routine sample analysis since the IDC study was completed. Alternatively, successful completion of an exclusively digested performance testing study result run since completing the IDC may be used.

16.1.2.3 Process CDC data using the same demonstration of capability spreadsheet and in the same manner as the IDC.

16.2 Method Detection Limit Studies

16.2.1 A Method Detection Limit (MDL) study must be performed annually for this procedure. The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence the value is above zero.

16.2.2 The procedure used for an MDL study is based on the method given in the Code of Federal Regulations, Title 40, Part 136, Appendix B, latest revision.

16.2.3 Seven replicate digestions are performed using laboratory reagent water spiked with the elements(s) of interest at the estimated minimum reportable concentration.

16.2.4 The standard deviation of the average for each element, using all seven results is calculated and multiplied by 3.143. The resulting number is the calculated MDL.

16.2.5 If the concentration spiked is between the calculated MDL and ≤10 times the calculated MDL, and there are no zero percent recoveries in the seven results then the MDL passes.

16.2.6 If the MDL study does not pass acceptably, it must be re-digested. If a study needs re-digested at a different concentration, the entire set of seven needs re-digested. If a study does not pass due to poor reproducibility on one result, only that one result needs re-digested. However, only one result of the seven can be re-digested without re-digesting the entire study.

16.2.7 All seven MDL study results do not need digested in the same digestion batch.

17.0 POLLUTION PREVENTION

17.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

17.2 Never dispose of a laboratory chemical without first referencing appropriate written instructions of disposal for that particular material.

17.3 Conserve the use of chemicals where applicable

17.4 Comply with all environmental laws associated with chemicals in the laboratory.

18.0 WASTE MANAGEMENT

18.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals. Material safety data sheets are located on the laboratory intranent library.

18.2 To minimize the environmental impact and costs associated with chemical disposal, order and use only the minimum amount of material required.

18.3 Follow all instructions in TriMatrix SOP GR-15-102 for laboratory waste disposal requirements.

19.0 REFERENCES

19.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846,* 3rd Edition, Final Update III, Revision 1, July 1992, Method 3010A, "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy"

19.2 *Code of Federal Regulations*, Title 40, Appendix C to Part 136, February 1, 2002, Method 200.7, "Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes"

20.0 ATTACHMENTS

20.1 ICP Spiking Solution SSW-1A Certificate of Analysis Example

20.2 ICP Spiking Solution SSW-SSS-2A Certificate of Analysis Example

20.3 Work Order Report Example

20.4 Preparation Batch Report Example

20.5 Digestion Flowchart

Attachment 20.1
ICP Spiking Solution SSW-1A Certificate of Analysis Example

INORGANIC VENTURES CERTIFICATE OF ANALYSIS

195 Lehigh Avenue, Suite 4
Lakewood, New Jersey 08701 · USA
inorganicventures.com

tel: 800.669.6799 · 732.901.1900
fax: 732.901.1903
info@inorganicventures.com

1.0 **INORGANIC VENTURES** is an ISO Guide 34:2000 registered Certified Reference Material (CRM) Manufacturer (Certificate #883-02). The certificate is designed and the data is determined in accordance with ISO Guide 31:2000 (Reference Materials-Contents of Certificates and Labels), ISO Guide 34:2000 "Quality System Guidelines for the Production of Reference Materials," and ISO Guide 35-1989 "Certification of Reference Materials - General and Statistical Principals."

2.0 **DESCRIPTION OF CRM** Custom Solution

Catalog No.: TRIMATRIX-SSW-1A

Lot Number: **Y-MEB188079**

Matrix: 2% HNO3(abs)

A607108
DA
7-06-06

2,500.00 µg/mL each:
Ca, K, Mg, Na,
250.00 µg/mL each:
Al, As, P, Se, Tl,
50.00 µg/mL each:
Ag, B, Ba, Cd, Co, Cr3, Cu, Fe, Li, Mn, Ni, Pb, Sr, V, Zn,
5.00 µg/mL each:
Be

3.0 **CERTIFIED VALUES AND UNCERTAINTIES**

ELEMENT	CERTIFIED VALUE	ELEMENT	CERTIFIED VALUE	ELEMENT	CERTIFIED VALUE
Aluminum, Al	249.8 ± 0.7 µg/mL	Arsenic, As	250.2 ± 0.8 µg/mL	Barium, Ba	50.16 ± 0.08 µg/mL
Beryllium, Be	5.004 ± 0.010 µg/mL	Boron, B	50.07 ± 0.10 µg/mL	Cadmium, Cd	50.16 ± 0.22 µg/mL
Calcium, Ca	2,500 ± 6 µg/mL	Chromium+3, Cr3	50.11 ± 0.16 µg/mL	Cobalt, Co	50.09 ± 0.12 µg/mL
Copper, Cu	50.17 ± 0.14 µg/mL	Iron, Fe	49.84 ± 0.32 µg/mL	Lead, Pb	50.17 ± 0.11 µg/mL
Lithium, Li	49.91 ± 0.06 µg/mL	Magnesium, Mg	2,501 ± 5 µg/mL	Manganese, Mn	49.97 ± 0.12 µg/mL
Nickel, Ni	50.10 ± 0.12 µg/mL	Phosphorus, P	249.5 ± 0.6 µg/mL	Potassium, K	2,500 ± 5 µg/mL
Selenium, Se	249.8 ± 0.8 µg/mL	Silver, Ag	50.01 ± 0.11 µg/mL	Sodium, Na	2,497 ± 1 µg/mL
Strontium, Sr	50.05 ± 0.11 µg/mL	Thallium, Tl	249.9 ± 0.7 µg/mL	Vanadium, V	49.98 ± 0.14 µg/mL
Zinc, Zn	50.09 ± 0.12 µg/mL				

Certified Density: 1.049 g/mL (measured at 22° C)

The Certified Value is based upon the most precise method used to analyze this CRM. The following equations are used in the calculation of the certified value and the uncertainty:

Certified Value $(\bar{x}) = \frac{\Sigma x_i}{n}$

Uncertainty $(\pm) = \frac{2[(\Sigma s_i)^2]^{1/2}}{(n)^{1/2}}$

$(\bar{x})$ = mean
x_i = individual results
n = number of measurements
Σs_i = The summation of all significant estimated errors
(Most common are the errors from instrumental measurement, weighing, dilution to volume, and the fixed error reported on the NIST SRM certificate of analysis.)

Approved By: 1-8-09 **QA Officer** **Approved By:** MAS 01/14/09 **Area Supervisor**

Attachment 20.2
ICP Spiking Solution SSW-SSS-2A Certificate of Analysis Example

INORGANIC VENTURES™ CERTIFICATE OF ANALYSIS

195 Lehigh Avenue, Suite 4
Lakewood, New Jersey 08701 · USA
inorganicventures.com
tel: 800.669.6799 · 732.901.1900
fax: 732.901.1903
info@inorganicventures.com

1.0 **INORGANIC VENTURES** is an ISO Guide 34:2000 registered Certified Reference Material (CRM) Manufacturer (Certificate #883-02). The certificate is designed and the data is determined in accordance with ISO Guide 31:2000 (Reference Materials-Contents of Certificates and Labels), ISO Guide 34:2000 "Quality System Guidelines for the Production of Reference Materials," and ISO Guide 35-1989 "Certification of Reference Materials - General and Statistical Principals."

2.0 **DESCRIPTION OF CRM** Custom Solution

Catalog No.: TRIMATRIX-SSW-SSS-2A

Lot Number: **Y-MEB201134**

Matrix: tr. HF, 2% HNO3(abs)

A6092280
DSL 9-11-06
exp. 10-01-07

250.00 µg/mL each:
Sb, Si, Sn,
50.00 µg/mL each:
Mo, Ti

3.0 **CERTIFIED VALUES AND UNCERTAINTIES**

ELEMENT	CERTIFIED VALUE	ELEMENT	CERTIFIED VALUE	ELEMENT	CERTIFIED VALUE
Antimony, Sb	249.1 ± 0.4 µg/mL	Molybdenum, Mo	50.02 ± 0.10 µg/mL	Silicon, Si	249.7 ± 0.8 µg/mL
Tin, Sn	250.6 ± 0.9 µg/mL	Titanium, Ti	50.14 ± 0.08 µg/mL		

Certified Density: 1.015 g/mL (measured at 22° C)

The Certified Value is based upon the most precise method used to analyze this CRM. The following equations are used in the calculation of the certified value and the uncertainty:

$$\text{Certified Value } (\bar{x}) = \frac{\Sigma x_i}{n}$$

$$\text{Uncertainty } (\pm) = \frac{2[(\Sigma s_i)^2]^{1/2}}{(n)^{1/2}}$$

($\bar{x}$) = mean
x_i = individual results
n = number of measurements
Σs_i = The summation of all significant estimated errors (Most common are the errors from instrumental measurement, weighing, dilution to volume, and the fixed error reported on the NIST SRM certificate of analysis.)

4.0 **TRACEBILITY TO NIST AND VALUES OBTAINED BY INDEPENDENT METHODS**

· "Property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties." (ISO VIM, 2nd ed., 1993, definition 6.10)

· This product is Traceable to NIST via an unbroken chain of comparisons. The uncertainties for each certified value are reported, taking into account the SRM uncertainty error and the measurement, weighing and volume dilution errors. In rare cases where no NIST SRMs are available, the term 'in-house std.' is specified.

Attachment 20.3
Work Order Report Example

TriMatrix Laboratories, Inc. **WORK ORDER 0609285** Printed: 9/20/2006 2:30:22PM

Page 1 of 2

Metals Sample Receipt Notice

Client: [redacted]
Project: **Analytical Services**
Client Due Date: **Oct-04-06 16:00 (10 day TAT)**
W.O. Comments: *1RL*

Project Manager: **Lisa M. Harvey**
Project Number: **32207**
Report Level: **1RL**

Lab Number	Sample Name / Analysis	Matrix	Sampled Date / TAT	Expire Date	Sample Comments / Lab Due Date	Comments
0609285-01	Powder Coat	Waste Water	Sep-19-06 00:00	Custom	metals,pH,TN	
	Ag Total 200.7		10	Mar-18-07 00:00	Oct-03-06 17:00	
	Cd Total 200.7		10	Mar-18-07 00:00	Oct-03-06 17:00	
	Cr Total 200.7		10	Mar-18-07 00:00	Oct-03-06 17:00	
	Cu Total 200.7		10	Mar-18-07 00:00	Oct-03-06 17:00	
	Ni Total 200.7		10	Mar-18-07 00:00	Oct-03-06 17:00	
	Pb Total 200.7		10	Mar-18-07 00:00	Oct-03-06 17:00	
	Zn Total 200.7		10	Mar-18-07 00:00	Oct-03-06 17:00	

Approved By: m 1-8-09 **QA Officer**
Approved By: MAS 01/14/09 **Area Supervisor**

Attachment 20.4
Preparation Batch Report Example

TriMatrix Laboratories, Inc. **PREPARATION BATCH** 0610868 Page 1 of 2 Printed: 9/22/2006 9:36:45AM

Metals, Waste Water, 3010A Digestion

Batch comments:
09/22/06 7:00am-3:30pm
Inst 219 #179 @ 95C
Hotblock Vessel Lot #A511LS106

Lab Number	Container	Prepared	By	Initial (mL)	Final (mL)	Client Source ID	Client Spike ID	Client uL Spike	Comments		
0609168-01	A	Sep-22-06 07:00	MAS	25	25	[redacted]					
Ag Total 200.7	Cd Total 200.7	Cr Total 200.7	Cu Total 200.7	Ni Total 200.7	Pb Total 200.7	Zn Total 200.7					
0609168-03	A	Sep-22-06 07:00	MAS	25	25	[redacted]					
Ag Total 200.7	Cd Total 200.7	Cr Total 200.7	Cu Total 200.7	Ni Total 200.7	Pb Total 200.7	Zn Total 200.7					
0609285-01	C	Sep-22-06 07:00	MAS	25	25	[redacted]					
Ag Total 200.7	Cd Total 200.7	Cr Total 200.7	Cu Total 200.7	Ni Total 200.7	Pb Total 200.7	Zn Total 200.7					
0609295-01	D	Sep-22-06 07:00	MAS	25	25	[redacted]					
Na Total 200.7											
0609300-04	A	Sep-22-06 07:00	MAS	25	25	[redacted]			report at 10 ug/L	report at 10 ug/L	
Cu Total 200.7											
0609303-01	B	Sep-22-06 07:00	MAS	25	25	[redacted]			Added for BatchQC in: 0610868	BatchQC	
Ag Total 200.7	Al Total 200.7	Cd Total 200.7	Cr Total 200.7	Cu Total 200.7	Mo Total 200.7	Na Total 200.7	Ni Total 200.7				
Pb Total 200.7	Zn Total 200.7										
0609304-01	B	Sep-22-06 07:00	MAS	25	25	[redacted]			wkly	wkly	
Cr Total 200.7	Cu Total 200.7	Ni Total 200.7	Zn Total 200.7								
0609305-01	A	Sep-22-06 07:00	MAS	25	25	[redacted]					
Ag Total 200.7	Al Total 200.7	Cd Total 200.7	Cr Total 200.7	Cu Total 200.7	Ni Total 200.7	Pb Total 200.7	Zn Total 200.7				
0609316-01	C	Sep-22-06 07:00	MAS	25	25	[redacted]					
Ag Total 200.7	Cd Total 200.7	Cr Total 200.7	Cu Total 200.7	Ni Total 200.7	Pb Total 200.7	Zn Total 200.7					
0609327-02	F	Sep-22-06 07:00	MAS	25	25	[redacted]					
Mo Total 200.7											
0609327-04	F	Sep-22-06 07:00	MAS	25	25	[redacted]					
Ag Total 200.7	Cd Total 200.7	Cr Total 200.7	Cu Total 200.7	Ni Total 200.7	Pb Total 200.7	Zn Total 200.7					
0609337-01	C	Sep-22-06 07:00	MAS	25	25	[redacted]					
Ag Total 200.7	Cd Total 200.7	Cr Total 200.7	Cu Total 200.7	Ni Total 200.7	Pb Total 200.7	Zn Total 200.7					

Comments:

Analyst Initials:

bch_TM_byAnalysis.rpt

Approved By: [illegible] 1-8-09 **QA Officer**

Approved By: MAS 01/14/09 **Area Supervisor**

Attachment 20.5
Digestion Flowchart

Measure 25.0 mL of homogeneous sample into a digestion vessel
↓
add 0.75 mL of concentrated nitric acid
↓
cover with a ribbed watchglass
↓
evaporate to about 1.25 mL at 90-95 deg. C (do not boil)
↓
remove from the block digestor to cool then add 1.25 mL concentrated nitric acid
↓
change to a non-ribbed watchglass and return to the block digestor
↓
reflux (slight boiling will be observed but vigorous boiling must be avoided)
↓
if the digestate is not light in color after refluxing, cool and add another 0.75 mL nitric acidthen continue refluxing as before
↓
repeat 0.75 mL nitric acid additions and refluxing until the digestion is complete
↓
remove from the block digestor and change to a ribbed watchglass
↓
evaporate to about 0.75 mL at 90-95 deg. C (do not boil)
↓
remove from the block digestor to cool then add 2.5 mL 1:1 hydrochloric acid
↓
change to a non-ribbed watchglass and return to the block digestor
↓
reflux gently for 15 minutes
↓
remove from the block digestor and cool to room temperature
↓
dilute to 25.0 mL with laboratory reagent water then cap and shake vigorously
↓
digestates are ready for analysis

Approved By: 1-8-09
QA Officer

Approved By: 01/14/09
Area Supervisor

TriMatrix Laboratories, Inc.

STANDARD OPERATING PROCEDURE

Block Digestion of Mercury in Soil, Waste and Oil

SW-846 Method 7471A

APPROVALS:

Area Supervisor: Marge A. Scott Date: 07-31-09
Marge A. Scott

QA Officer: Date: 7-31-09
Tom C. Boocher

Operations Manager: Date: 8/3/09
Jeff P. Glaser

Procedure Number: GR-01-139
Revision Number: 0.2

Date Initiated: 5/19/03
Effective Date: 8/15/09

Date Revised: 7/31/09
Pages Revised: All

By: Marge A. Scott
Total Number of Pages: 15

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

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1.0 SCOPE AND APPLICATION

1.1 This procedure outlines the preparation of total mercury (inorganic and organic) in soil, waste and oil samples. All samples analyzed must undergo this digestion before analysis.

2.0 PRINCIPAL METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition.* Final Update III, Revision 1, September 1994, Method 7471A, "Mercury in Solid or Semi-Solid Waste (Manual Cold-Vapor Technique)"

3.0 SUMMARY OF PROCEDURE

3.1 A measured sample mass is block-digested for two minutes with aqua regia. The digestion breaks down organo-mercury compounds into mercury in the Hg^{2+} state.

4.0 PARAMETER OR COMPOUND LIST

4.1 Mercury

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal,* latest revision

5.2 TriMatrix SOP GR-09-128, *Homogenization, Grinding and Drying of Solid Samples*, latest revision

5.3 TriMatrix SOP GR-01-123, *Mercury in Aqueous and Solid Samples, Atomic Absorbance, semi-Automated Cold Vapor*, latest revision

5.4 TriMatrix SOP GR-10-106, *Inorganic and Metals Laboratories Corrective Actions*, latest revision

5.5 TriMatrix SOP GR-10-125, *Method Detection Limit (MDL)*, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Soil samples often contain mercury at low concentration. When soils are mixed and ground, the possibility that liquid samples may become cross-contaminated exists and/or cause a health hazard. Therefore, soils must be mixed and ground in the fume hood and the soil preparation area must be kept free of dust and dirt.

6.2 If a mercury thermometer is broken anywhere in the laboratory, the metals lab must be notified.

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6.3 Mercury may be lost if the block digestor is hotter than 95° C. Digestions must be temperature monitored with a NIST-verified thermometer and the temperature recorded on the pretreatment benchsheet. If sample digestion occurs above 95° C, the sample batch must be re-digested. Refer to Attachment 20.2 for an example preparation batch report.

6.4 Reagents used in this procedure will become contaminated over time. If contamination is suspected in a reagent before the established expiration, the reagent must be discarded and fresh made.

6.5 Potassium permanganate is added to eliminate possible interference from sulfide as sodium sulfide.

6.6 Copper has been reported to interfere at concentrations above 10 mg/L in the digestate.

6.7 Samples high in chlorides and volatile organic materials require additional permanganate which must also be added to standards and quality control.

7.0 SAFETY PRECAUTIONS

7.1 Analysts must comply with all instructions for health and safety as outlined in the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan.

7.2 Concentrated acids are used in the preparation of standards and samples for mercury analysis. Gloves, labcoats and safety glasses must be worn at all times when handling concentrated acids. Gloves must also be worn when handling digested samples. Refer to the material safety data sheet (MSDS) for information on these or other chemicals utilized in this procedure.

7.3 Mercury exists in many forms and is toxic in a variety of ways. Mercury vapor is toxic if inhaled. Do not operate the block digestor if it is not properly ventilated. Elemental Hg and Hg^{2+} are toxic if ingested. Always wash hands after handling the mercury solutions.

7.4 No food or drink is allowed in the metals lab. Food or drink may become contaminated with acid or metals and will be considered hazardous. Any food or drink found in the metals laboratory must be disposed of and not eaten.

7.5 Wash hands before starting work. Chemicals may be present on the skin that interferes with mercury analysis. Wash hands before leaving the metals lab as well. Chemicals and acids may be on the skin that could eventually be ingested or passed on through casual contact.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Soil, waste and oil samples must be refrigerated. The maximum holding time for non-aqueous samples for mercury is 28 days from the time of collection.

8.2 The minimum sample size for mercury analysis is 10 g to ensure enough sample volume for quality control.

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9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Balance, analytical, capable of measurement to 0.0001 g

9.2 Balance, top-loading, capable of measurement to 0.1 g

9.3 Autopipettor, capable of delivering 50 - 1,000 µL

9.4 Volumetric flasks, class A, various volumes

9.5 Block digestor, Environmental Express, HotBlock™

9.6 Digestion vessels, Environmental Express, HotBlock™, cat. SC475, certified accurate to 50 ±0.2 mL

9.7 Millipore, in-line filters, Millex HPF HV 0.45 µm, PVDF 25 mm, non-sterile, cat. SLHVM25NS

9.8 Thermometer, metal-stem, digital, NIST-verified, Fisher model 14-648-12 (or equivalent), capable of reading from -50 to 150° C. Do not use a mercury thermometer.

9.9 Incubator, Boekel, model 131400, temperature range 50 - 60° C

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Verify and document the autopipetter calibration daily.

10.2 Clean the block digestor and counters daily or more frequently when minor spills occur.

10.3 Verify balance calibrations and document in the Daily Balance Calibration Logbook daily.

11.0 CHEMICALS AND REAGENTS

11.1 Acids used in standards preparation and for sample processing must be trace-metal grade or better.

11.1.1 Concentrated hydrochloric acid, trace-metal grade (HCl)

11.1.2 Concentrated nitric acid, trace-metal grade (HNO_3)

11.2 Reagent water: ASTM Type II laboratory water prepared for mercury analysis is deionized water fed into an all-glass distillation unit. The resulting distillate is immediately placed in a plastic container and capped. This is the ONLY water acceptable for use in the metals lab.

11.3 Aqua Regia

11.3.1 In a glass bottle, slowly add three volumes of concentrated HCl to one volume of concentrated HNO_3.

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Note: Aqua regia must be prepared and used only in a hood.

11.4 Potassium permanganate solution (ACS grade), 5% (w/v)

11.4.1 In a plastic 3-liter container, place 50 g $KMnO_4$ crystals. Add 1 liter metals reagent water to the container.

11.4.2 Place a stir bar in the solution and stir on a magnetic stir plate without heat until all crystals have dissolved. Use a disposable glass pipet to probe the container bottom for excess crystals. If crystals are found, keep stirring as this is nearly a saturated solution and may take several hours to prepare. This reagent must be made fresh daily.

11.4.3 Update the reagent logbook for each batch made.

11.4.4 If any permanganate solution spills, clean it up immediately with water. If a brownish stain develops on a contacted surface, remove it with a dilute solution of hydroxylamine hydrochloride.

Note: If permanganate touches exposed skin, a brownish stain will develop. Wash the excess permanganate off immediately for 15 minutes. If splashed in the eye, wash for 15 minutes and notify laboratory management. Read the MSDS before using this chemical.

11.4.5 Potassium permanganate will collect mercury if left exposed to the atmosphere. The solution must be kept in a sealed container when not in use and must be stored in a dark cabinet to reduce the potential for auto-catalytic reduction.

11.4.6 At no time must permanganate be exposed to organic materials or reducing agents outside the scope of this procedure. A fire or explosion could result. Do not let the solution dry and form crystals on any surface or in any container.

11.5 Sodium chloride/hydroxylamine hydrochloride solution, 12% (w/v)

11.5.1 In a plastic 3-liter container, place 60 g of sodium chloride and 60 g of hydroxylamine hydrochloride.

11.5.2 Add 500 mL of metals reagent water and a stir bar. Place the container on a stir plate without heat and stir until all crystals have dissolved. This reagent must be prepared fresh daily.

11.5.3 Update the reagent logbook for each batch made.

12.0 STANDARDS PREPARATION

12.1 The mercury stock solution for calibration is purchased commercially at a concentration of 1,000 mg/L. The second-source calibration verification (SCV) solution is purchased commercially at 1,000 mg/L from an alternate vender. All purchased standards are single-element solutions, certified to be NIST-traceable.

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12.1.1 Purchased standards have an expiration date of one year from the date received unless otherwise specified by the vender. Whichever is sooner.

12.1.2 When received in the laboratory, record in the Standards Logbook (Attachment 20.4), giving each standard a unique book/line/page identifier.

12.1.3 All intermediate and working standards must be replaced daily. These standards do not need recorded in the Standards Logbook. However, all preparation details and the purchased standard identifier must be recorded on the analytical benchsheet.

12.2 Prepare a 1000 ug/L intermediate solution as follows:

12.2.1 Rinse a clean 100 mL volumetric flask with metals reagent water, several times.

12.2.2 Place about 20 mL of metals reagent water in the volumetric.

12.2.3 Pipet 0.5 mL concentrated trace-metal grade HNO_3 into the volumetric and swirl.

12.2.4 Pipet 100 µL of 1,000 mg/L purchased mercury solution into the volumetric.

12.2.5 Dilute to the mark with metals reagent water. Cap and mix well.

12.2.6 Record in the standards logbook and write the book/page/line identifier on the volumetric flask.

12.3 Calibration Standards

12.3.1 Six concentrations are prepared for use in the initial calibration curve. These typically include a blank, a low-level at the reporting limit (0.2 ug/L), three mid-levels and a high-level near the upper linear range (5.0 ug/L).

12.3.1 Calibration standards are first prepared by rinsing six clean 50 mL block digestion vessels several times with metals reagent water. Label as 5.0 ug/L Hg, 2.0 ug/L Hg, 1.0 ug/L Hg, 0.5 ug/L Hg, 0.2 ug/L Hg, 0.0 ug/L Hg.

12.3.2 Add approximately 2.5 mL metals reagent water to each volumetric.

12.3.3 Pipet 0.25 mL concentrated trace-metal grade HNO_3 to each and swirl.

12.3.4 Pipet 250 µL of the 1,000 ug/L mercury standard (Section 12.2) into the 50 mL flask labeled 5.0 ug/L Hg.

12.3.5 Pipet 100 µL of the 1,000 ug/L Hg standard (Section 12.2) into the 50 mL flask labeled 2.0 ug/L Hg.

12.3.6 Pipet 50 µL of the 1,000 ug/L Hg standard (Section 12.2) into the 50 mL flask labeled 1.0 ug/L Hg.

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12.3.7 Pipet 25 µL of the 1,000 ug/L Hg standard (Section 12.2) into the 50 mL flask labeled 0.5 ug/L Hg.

12.3.8 Pipet 10 µL of the 1,000 ug/L Hg standard (Section 12.2) into the 50 mL flask labeled 0.2 ug/L Hg.

12.3.9 Add 2.5 mL metals reagent water to the flask labeled 0.0 ug/L Hg.

12.3.10 Digest in accordance with Sections 13.6 through 13.13.

12.4 Preparation of the second-source calibration verification (SCV) is as follows:

12.4.1 Prepare a second-source 1000 ug/L intermediate solution as follows:

12.4.1.1 Add about 20 mL of metals reagent water and pipet 0.5 mL concentrated HNO_3 into a 100 mL volumetric flask. Swirl to mix.

12.4.1.2 Pipet 100 µL of the secondary 1,000 mg/L stock into the flask and dilute to volume with metals reagent water.

12.4.2 Preparation of the 3.0 ug/L SCV is as follows:

12.4.2.1 Rinse a clean 50 mL block digestion vessel several times with metals reagent water and label it "SCV".

12.4.2.2 Add approximately 2.5 mL metals reagent water.

12.4.2.3 Pipet 250 µL concentrated HNO_3 into the flask and swirl.

12.4.2.4 Pipet 150 µL of the 1,000 ug/L solution (Section 12.5.1) into the vessel.

12.4.2.5 Digest in accordance with Sections 13.6 through 13.13.

12.5 Matrix Spiking

12.5.1 Samples need Matrix Spiked (MS/SPK) and Matrix Spike Duplicated (MSD/SPK) at a frequency of 5% or with each digestion batch of up to 20 samples. Prepare a separate MS/MSD for each matrix digested within a sample batch (soil, waste, oil or unknown).

12.5.1.1 Prepare two duplicate digestion vessels of sample to be spiked by following Sections 13.2 through 13.4.

12.5.1.2 Add 100 µL of 1,000 ug/L Hg (Section 12.5.1) to each vessel.

12.5.1.3 Digest in accordance with Sections 13.5 through 13.13.

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12.5.2 A Blank Spike (LFB/BS) is prepared with each digestion batch of up to 20 samples.

12.5.2.1 Prepare a blank spike by pipetting 100 µL of 1,000 ug/L Hg (Section 12.4.1) into a digestion vessel .

12.5.2.2 Place the vessel into the drying oven at 50-60° C in accordance with TriMatrix SOP GR-01-115.

12.5.2.3 Digest in accordance with Sections 13.5 through 13.13.

13.0 ANALYTICAL PROCEDURE

13.1 All calibration standards, quality control and client samples must be digested before analysis.

13.2 Rinse all digestion vessels and caps with metals reagent water before use.

13.3 Dry and homogenize all soils and solid waste before digesting according to TriMatrix SOP GR-01-115. Do not attempt to dry oil samples.

13.4 Weigh three separate aliquots of homogeneously mixed sample (dried, if not an oil) into a digestion vessel. The total of the three weighings must be 0.3000 ± 0.0005 g.

13.5 Add 2.5 mL of metals reagent water.

13.6 Pipet 2.5 mL aqua regia into the vessel.

13.7 Position a cap loosely on the vessel and heat at 90-95° C for 2 minutes in the block digestor.

13.8 Remove and let cool for 10 minutes then add 25 mL metals reagent water and 7.5 mL 5% $KMnO_4$ then let stand for 15 minutes. If a digestate does not maintain the purple or brown color associated with excess permanganate, discard it and weigh out a smaller total aliquot to digest. After cooling from the permanganate addition, screw the cap on.

13.9 Return to the block digestor and digest with the cap screwed on for 30 minutes at 90-95° C.

13.10 After digestion, let cool to room temperature and add 3.0 mL 12% $NaCl/NH_2OH$ then cap and shake. If the permanganate color does not clear, incrementally add 0.5 mL of the 12% $NaCl/NH_2OH$ solution until all permanganate color is gone.

13.11 When the permanganate color is gone, dilute to 50 mL with metals reagent water in the digestion vessel (each is calibrated to 50 mL) then cap and mix.

13.12 All digestates need shaken immediately before analysis. If a delay occurs between setting up and running, re-shake the entire batch to prevent layering. All sample and matrix control digestates (samples, digestion blanks, blank spikes and matrix spikes) need passed through a 0.45 µm filter immediately before analysis

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13.13 After filtering (when necessary) digestates are ready for analysis.

14.0 DATA REPORTING AND DELIVERABLES

14.1 The analyst is responsible for data quality and for correctly filling in the proper documentation. This is required for quality control and to provide the client with defensible data.

14.2 Laboratory information management system (LIMS) reporting is as follows:

14.2.1 When the analyst has finished a batch analysis all data must be input to Element™, the laboratory information management system. Benchsheets must be filled in completely to insure that results are reported correctly and all data is associated with the right quality control batch.

14.2.2 If internal chain-of-custody is required it is very important the COC form be filled in correctly.

14.2.3 All benchsheets (including COC forms) must be filed in the project-specific raw data folder.

14.3 Laboratory Required Paperwork

14.3.1 All logbooks must be filled in completely and correctly.

14.3.2 All corrections are to be made in indelible ink.

14.3.3 **Corrections are to be made with a single lineout which is then dated and initialed. Write-overs are not acceptable.** Each erroneous result must remain legible. The new result must be placed near the incorrect result.

14.3.4 Blank lines in logbooks must be Z'd out.

15.0 QUALITY ASSURANCE

15.1 One digestion blank (MPB/BLK) is carried through the entire digestion to monitor contamination for each analysis batch. The blank is prepared in the same way as a sample using an empty digestion vessel.

15.2 One blank spike (LFB/BS) is carried through the entire digestion to monitor recovery efficiency using an empty digestion vessel. Refer to Section 12.5.2 for a detailed description on how to prepare.

15.3 Matrix Spike/Matrix Spike Duplicates are performed at a frequency of 5% or for each batch of up to 20 samples per matrix, to monitor matrix recovery efficiency. Refer to Section 12.5.1 for a detailed description on how to prepare.

15.4 Digestions must not boil. If a digestion begins boiling, immediately remove it from the block digestor and lower the temperature. Replace the digestion at the lower temperature and continue digesting at 90-95° C.

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15.5 Ensure that the spiking solution used is within the expiration date by checking the standards log or the label. If a spiking solution has expired, do not use and prepare another.

16.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

16.1 Before processing actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running an acceptable Initial Demonstration of Capability (IDC). Annually, a Continuing Demonstration of Capability (CDC) is required.

16.1.1 Initial Demonstration of Capability

16.1.1.1 Prepare four blank spikes at 0.417 mg/kg Hg in empty digestion vessels. The spiking solution used must be prepared independently from the calibration standards. Digest following every requirement in the procedure. Analyze the IDC study by calculating average percent recovery and standard deviation using the IDC spreadsheet located on the laboratory intranet library. Average percent recovery must fall within established blank spike quality control acceptance limits. The standard deviation must be ≤20%.

16.1.1.2 Alternatively, the last four of seven results obtained from an MDL study may be used as the IDC if the MDL study was run exclusively by the analyst. ONLY the last four of the seven results may be used.

16.1.1.3 If these IDC criteria are not met, locate and correct the source of the problem and repeat the study. Repeated failure however, will confirm a general problem with the procedure or techniques used. If this occurs, locate the problem and correct the procedure or techniques used then repeat the study.

16.1.1.4 Samples may not be processed by any analyst or on any new instrument until an IDC study has been successfully completed.

16.1.1.5 Copies of successful IDC and/or instrument validation spreadsheets and raw data must be given to Quality Assurance for documentation and generation of training forms.

16.1.2 Continuing Demonstration of Capability

16.1.2.1 Annually, a Continuing Demonstration of Capability (CDC) is required by each analyst.

16.1.2.2 The CDC may be accomplished by repeating the IDC, by using the last four results from the annual MDL study if run exclusively by the analyst or by processing four consecutive blank spikes run exclusively by the analyst during the course of routine sample digestion.

16.1.2.3 Process all CDC data using the same spreadsheet used for the IDC study.

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16.1.2.4 Alternatively, the successful completion of a Performance Testing sample analyzed exclusively by the analyst during the preceding year may be used for a CDC.

16.2 A Method Detection Limit study is required annually in accordance with TriMatrix SOP GR-10-125.

17.0 POLLUTION PREVENTION

17.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

17.2 Never dispose of laboratory chemicals without first referencing appropriate written disposal instructions, for that particular material. Absolutely no mercury is to be disposed of in the laboratory sink.

17.3 Conserve the use of chemicals where applicable.

17.4 Comply with all environmental laws associated with chemicals in the laboratory.

18.0 WASTE MANAGEMENT

18.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals. All MSDS information is maintained on the laboratory intranet library.

18.2 To minimize the environmental impact and costs associated with chemical disposal, order and use only the minimum amount of material required.

18.3 Follow all instructions in TriMatrix SOP GR-15-102 for laboratory waste disposal requirements.

19.0 REFERENCES

19.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 1, September, 1994, Method 7471A, "Mercury in Solid or Semi-Solid Waste (Manual Cold-Vapor Technique)"

20.0 ATTACHMENTS

20.1 Purchased Mercury Stock Standard Certificate of Analysis

20.2 Example Preparation Batch Report

20.3 Example Analysis Sequence Report

20.4 Example Stock Standards Logbook

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Attachment 20.1
Purchased Mercury Stock Standard Certificate of Analysis

HIGH-PURITY STANDARDS

CAT.NO.100033-1

Certificate of Analysis

Mr 13.97.16
DR
7-29-04

Mercury

Lot # 413140

Source	Source Purity	Matrix	Density g/mL @ 21.9°C	Standard Concentration
Mercury Metal	99.998%	HNO_3, 2%	1.0125	1000 ± 3 µg/mL

This spectrometric standard solution has been prepared from high-purity reference materials. Subboiled high-purity acid has been used to place the materials in solution and to stabilize the standard. The matrix is as noted above in 18 megaohm deionized water. The reference materials have been assayed by optical emission spectrometry and atomic absorption spectrometry

The Mercury was analyzed by ICP-MS for trace impurities. The less than values are detection limits for the method. M=Major element.

Concentrations as µg/L (ppb)

Li	<0.02	Be	<0.02	B	<1.0	Na	<1.0	Mg	<0.02	Al	<1.0	Si	<1.0	K	<1.0
Ca	<1.0	Sc	<0.02	Ti	<0.02	V	<0.02	Cr	<0.02	Mn	<0.02	Fe	<1.0	Co	<0.02
Ni	<0.02	Cu	<0.02	Zn	<0.02	Ga	<0.02	Ge	<0.02	As	<0.02	Se	<0.02	Rb	<0.02
Sr	<0.02	Y	<0.02	Zr	<0.02	Nb	<0.02	Mo	<0.02	Ru	<0.02	Rh	<0.02	Pd	<0.02
Ag	200.0	Cd	<0.02	In	<0.02	Sn	<0.02	Sb	<0.02	Te	<0.02	Cs	<0.02	Ba	<0.02
La	<0.02	Ce	<0.02	Pr	<0.02	Nd	<0.02	Sm	<0.02	Eu	<0.02	Gd	<0.02	Tb	<0.02
Dy	<0.02	Ho	<0.02	Er	<0.02	Tm	<0.02	Yb	<0.02	Lu	<0.02	Hf	<0.02	Ta	<0.02
W	<0.02	Re	<0.02	Os	<0.02	Ir	<0.02	Pt	3.0	Au	8.0	Hg	M	Tl	<0.02
Pb	<0.02	Bi	<0.02	Th	<0.02	U	<0.02								

The Standard Concentration has been certified by spectrometric analysis against an independent source which is directly traceable to National Institute of Standards and Technology, Standard Reference Material No. 3133.

This standard is valid for eighteen months from the shipping date provided the solution is kept tightly capped and stored under normal laboratory conditions.

Theodore C. Rains

Theodore C. Rains, Ph.D.
President

Exp. Date FEB 2006

MSDS ATTACHED

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Attachment 20.2
Example Preparation Batch Report

TriMatrix Laboratories, Inc.

PREPARATION BATCH 0612013 Page 1 of 1

Printed: 3/30/2007 4:35:55PM

Metals, Soil, 7471A Mercury Digestion
(No Surrogate)
Batch Comments: MAS 10/16/06 2:00-2:30PM

Work Order	Analysis	Work Order	Analysis	Work Order	Analysis
0610275	Hg Total 7471A	0610276	Hg Total 7471A		

Lab Number	Contain	Prepared	By	Initial (g)	Final (mL)	uL Surrogate	Source ID	Spike ID	uL Spike	Client / QC Type	Extraction Comments
0612013-BLK1		Oct-16-06 14:00	MAS	0.3	50					BLANK	
0612013-BS1		Oct-16-06 14:00	MAS	0.3	50			A606452	100	LCS	
0612013-MS1		Oct-16-06 14:00	MAS	0.3	50		0610275-03	A606452	100	MATRIX SPIKE	
0612013-MSD1		Oct-16-06 14:00	MAS	0.3003	50		0610275-03	A606452	100	MATRIX SPIKE DUP	
0610275-01	A	Oct-16-06 14:00	MAS	0.2995	50					[redacted]	
0610275-03	A	Oct-16-06 14:00	MAS	0.3003	50					[redacted]	
0610275-04	A	Oct-16-06 14:00	MAS	0.2999	50					[redacted]	
0610275-05	A	Oct-16-06 14:00	MAS	0.3003	50					[redacted]	
0610276-01	A	Oct-16-06 14:00	MAS	0.2995	50					[redacted]	
0610276-02	A	Oct-16-06 14:00	MAS	0.2998	50					[redacted]	
0610276-03	A	Oct-16-06 14:00	MAS	0.2996	50					[redacted]	
0610276-04	A	Oct-16-06 14:00	MAS	0.2997	50					[redacted]	
0610276-05	A	Oct-16-06 14:00	MAS	0.3005	50					[redacted]	
0610276-06	A	Oct-16-06 14:00	MAS	0.3005	50					[redacted]	
0610276-07	A	Oct-16-06 14:00	MAS	0.2999	50					[redacted]	
0610276-08	A	Oct-16-06 14:00	MAS	0.2998	50					[redacted]	
0610276-09	A	Oct-16-06 14:00	MAS	0.3005	50					[redacted]	

Comments	Analyst Initials

bch_TriMatrix.rpt

Approved By: pm 7-31-09
QA Officer

Approved By: Tna Scott
Area Supervisor

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Attachment 20.3
Example Analysis Sequence Report

TriMatrix Laboratories, Inc. ANALYSIS SEQUENCE 7032613 Page 1 of 2 Printed: 3/30/2007 4:53:36PM

Metals, Soil, Mar-23-07

Instrument = 216, Calibration = UNASSIGNED

Sequence Analyses:
Hg Total 7471A

Lab Number	*Analysis*	*Contain*	*STD ID*	*ISTD ID*	*Client / QC Type*	*Extraction Comments*
7032613-ICV1	QC		7030390		INITIAL CAL CHECK	
7032613-SCV1	QC		6120277		SECONDARY CAL CHECK	
7032613-ICB1	QC		7030388		INITIAL CAL BLANK	
7032613-CRL1	QC		7030393		MRL CHECK	
7032613-CCV1	QC		7030390		CALIBRATION CHECK	
7032613-CCB1	QC		7030388		CALIBRATION BLANK	
0702875-BLK1	QC				BLANK	
0702875-BS1	QC				LCS	
0703212-05	Hg Total 7471A	A 07			[redacted]	From 0702697 by MAS on Mar-21-07
0702875-MS1	QC				MATRIX SPIKE	
0702875-MSD1	QC				MATRIX SPIKE DUP	
0703291-01	Hg Total 7471A	A 07			[redacted]	soil
0702875-MS2	QC				MATRIX SPIKE	
0702875-MSD2	QC				MATRIX SPIKE DUP	
0702874-BLK1	QC				BLANK	
0702874-BS1	QC				LCS	
7032613-CCV2	QC		7030390		CALIBRATION CHECK	
7032613-CCB2	QC		7030388		CALIBRATION BLANK	
0703320-01	Hg Total 7471A	A 02			[redacted]	soil
0702874-MS1	QC				MATRIX SPIKE	
0702874-MSD1	QC				MATRIX SPIKE DUP	
0703320-02	Hg Total 7471A	A 02			[redacted]	soil
0703320-03	Hg Total 7471A	A 02			[redacted]	soil

Comments:

Analyst Initials:

seq_TriMatrix.rpt

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Attachment 20.4
Example Stock Standards Logbook

TriMatrix Laboratories, Inc.

Row #	Standard Number	Standard Description	Analyte(s) (and/or Stock Standard Number for dilutions)	Manufacturer and Lot Numbers	Exp. Date	Ampule or Stock Standard Concentration	Initial Weight/ Volume	Solvent Used/ Lot #	Final Volume	Final Concentration	Made or Opened By	Date Made or Opened	Date Expires	Math Check By
1	ME12.25-1	50	ME11.43.1 ME11.43.2	—	4/1/04	100 mg/L	50 ml	ME12.24.19	100 ml	50 mg/L	JMJ	4/14/03	4/14/03	
2	ME12.25-2	20	↓	—	↓	↓	20 ml	↓	↓	20	↓	↓	↓	
3	ME12.25-3	10	↓	—	↓	↓	10 ml	↓	↓	10	↓	↓	↓	
4	ME12.25-4	1.0	ME12.24.13	—	4/18/03	~~10 mg/L~~ 100 mg/L	1 ml	↓	↓	1.0	↓	↓	↓	
5	ME12.25-5	~~0.04~~ 0.2	↓	—	↓	↓	20 ml	↓	↓	0.2	↓	↓	↓	
6	ME12.25-6	0.04	↓	—	↓	↓	40 ml	↓	↓	0.04	↓	↓	↓	
7	ME12.25-7	LCS	ME12.11.12	—	4/1/03	~~100 mg/L~~ 100 mg/L	400 ml	↓	↓	40	↓	↓	↓	
8	ME12.25-8	Hg ICS	ME11.4.18	CE 226003	4/01/03	1000 ug/ml	1.0 ml	ASTM II	100 ml	10,000 ppb	MSS	04/01/03	04/02/03	
9	ME12.25-9		HNO3	F 1102100	03/01/05	Conc	0.5 ml	↓	↓	0.5%	↓	↓	↓	
10	ME12.25-10	Hg	ME10.46.13	IV J:#603030	10/01/03	992 ug/ml	1.0 ml	ASTM II	100 ml	10,000 ppb	MSS	04/01/03	04/01/03	
11	ME12.25-11		HNO3	F 1102100	03/01/05	Conc	0.5 ml	↓	↓	0.5%	↓	↓	↓	
12	ME12.25-12													
13	ME12.25-13	Icpms spk 19A	ME10.3.15	IV THEB 130121	08/01/03	135 ug/ml	4.0 ml	ASTM II	100 ml	5 ug/ml	DSC	07/14/03	08/01/03	
14	ME12.25-14	Icpms spk 5A	ME10.3.14	IV THEB 130120	08/01/03	↓	↓	↓	↓	↓	↓	↓	↓	
15	ME12.25-15	Hg	CE 234711	CE 234711	04/01/04	—	—	—	—		MSS	04/14/03	04/14/03	
16	ME12.25-16	Hg	ME11.4.18	CE 226003	11/01/03	1000 ug/ml	1.0 ml	ASTM II	100 ml	10,000 ppb	MSS	04/14/03	04/15/03	
17	ME12.25-17		HNO3	F 1107100	3/1/05	Conc	0.5 ml	↓	↓	0.5%	↓	↓	↓	
18	ME12.25-18													

Approved By: 7-31-09
QA Officer

Approved By: Ma Scott
Area Supervisor

TriMatrix Laboratories, Inc.

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STANDARD OPERATING PROCEDURE

Mercury in Water by Oxidation, Purge and Trap, Cold Vapor Atomic Fluorescence Spectrometry

EPA Method 1631E

APPROVALS:

Area Supervisor: Denise Coffey Date: 1-19-09
Denise S. Coffey

QA Officer: Date: 1-8-09
Tom C. Boocher

Operations Manager: Jeff P. Glaser Date: 1/19/09
Jeff P. Glaser

Procedure Number: GR-01-138
Revision Number: 0.6

Date Initiated: 2/13/02
Effective Date: 1/20/09

Date Revised: 1/7/09
Pages Revised: All

By: David W. Johnson
Total Number of Pages: 23

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

1.0 SCOPE AND APPLICATION

1.1 This procedure is for the trace level determination of total and dissolved mercury in drinking water, wastewater, groundwater and aqueous waste.

1.2 The technique for pretreatment and analysis is BrCl oxidation, purge and trap, then desorption to Cold Vapor Atomic Fluorescence Spectrometry (CVAFS).

1.3 The analytical range is 0.5 ng/L to 10 ng/L. The range can be extended by reduction of sample volume used and calibration over a higher concentration range.

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry,* Method 1631, Revision E: August 2002, USEPA, Office of Water Publication, EPA-821-R-02-019

3.0 SUMMARY OF PROCEDURE

3.1 Before analysis, the mercury in all samples, standards and quality control must be oxidized as described in Section 13.0. The oxidation step breaks organomercury complexes to release mercuric ion (Hg^{2+}).

3.2 After oxidation, mercuric ion is introduced into the instrument in an HCl carrier flow. The liquid flow enters a gas-liquid separator where it is mixed with stannous chloride which reduces mercuric ion to elemental mercury (Hg^0) in a cold vapor, according to the following reaction:

$$Hg^{2+} + Sn^{2+} \rightarrow Hg^0 + Sn^{4+}$$

3.3 Argon is introduced into the separator to carry the cold vapor through a hygroscopic membrane and over a gold-plated wire, which traps the elemental mercury.

3.4 The wire is thermally heated in an argon gas flow, desorbing the trapped Hg^0 into an Atomic Fluorescence Spectrometer (CVAFS) detector cell. Quantitation is performed against known mercury standards.

4.0 PARAMETER OR COMPOUND LIST

4.1 Mercury

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal,* latest revision

5.2 PSA Millennium Merlin/Galahad Operating Manual

5.3 PSA Analytical Operating Manual

5.4 TriMatrix SOP GR-10-123, *Element Data Transfer and Review*, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Gold and iodide are known interferences.

6.2 Soil often contains mercury at trace levels. Soil samples are mixed and ground in the laboratory and can contaminate by becoming airborne particles, unless special precautions are taken. Sample preparation areas must be dusted and all soil removed before preparing water samples for trace level mercury analysis.

6.3 If a mercury thermometer is broken anywhere in the laboratory, the metals laboratory must be notified as trace levels of airborne mercury from the spill can easily spread. If airborne contamination is suspected, discard and re-prepare all samples, standards and reagents.

6.4 Reagents used in this procedure may become contaminated over time. If contamination is suspected or observed in blanks, all reagents must be discarded and remade.

7.0 SAFETY PRECAUTIONS

7.1 Analysts must comply with all instructions for health and safety as outlined in the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan.

7.2 Disposable gloves, safety glasses and a laboratory coat must be worn at all times when working in the metals laboratory. Concentrated acids, oxidizers, reagents and oxidized samples can produce serious burns or injuries. Refer to the MSDS library for information on chemicals used in this procedure.

7.3 Check to ensure the instrument exhaust system is connected and filtering through activated charcoal. If the exhaust is not working, immediately contact the metals laboratory supervisor. Under no circumstances must the unit be operated if the exhaust is not functioning properly.

7.4 The analytical instrument uses argon. Although argon gas is not hazardous or flammable, it can suffocate through oxygen deprivation. It is imperative that all sources of argon be turned off at the source valve when not in use.

7.5 Mercury exists in many forms, and is toxic in a variety of ways. Mercury vapor is toxic if inhaled. Hg^{2+} is toxic, if ingested. Chronic mercury exposure can cause kidney damage, muscle tremors, spasms, personality changes, depression, irritability and nervousness. Organomercury compounds can cause permanent brain damage. All standards must be prepared in a laboratory fume hood. Disposable gloves, safety glasses and laboratory coats must be worn at all times when working in the metals laboratory.

7.6 No food or beverages are allowed in the metals laboratory.

7.7 Wash hands before starting work. Chemicals may be present on the skin that can interfere with trace level mercury analysis. Wash hands before leaving the metals laboratory. Chemicals and acids may be on the skin that could be ingested or passed to others through casual contact.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Samples must be collected in cleaned 40 mL borosilicate glass vials with PTFE-lined lids.

8.1.1 Two vials are collected for each sample. If matrix QC is to be performed on the sample an additional two vials will be collected at the same time.

8.1.2 A 300 mL cleaned borosilicate glass bottle with PTFE-lined cap will be sent out to use as an equipment blank. Analyze the equipment blank and inform the project chemist if above the reporting limit.

8.1.3 Field/Trip blanks are sent with each sampling set. Analyze field/trip blanks and inform the project chemist if above the reporting limit.

8.2 Samples are preserved, by adding BrCl solution. Preserved samples are stable for 90 days and must be analyzed within that hold time. Samples may be shipped to the laboratory unpreserved with the following conditions:

8.2.1 They must be completely filled without headspace.

8.2.2 They must be capped tightly.

8.2.3 They must be oxidized within 48 hours of sampling. If a sample is oxidized in the same vial, the hold time can be extended to 28 days.

8.3 All samples, standards and quality control must be subjected to the oxidation step detailed in Section 13.0, before analysis.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Analytical balance, capable of weighing 0.1 mg

9.2 Balance, capable of weighing 0.1 g

9.3 Micropipettors, capable of delivering 10-100 µL

9.4 Micropipettors, capable of delivering 100-1000 µL

9.5 Macropipettors, capable of delivering 5-10 mL

9.6 Centrifuge tubes (50 mL), capable of fitting into the PS Analytics autosampler.

9.7 PSA, model 10.035 Millennium Merlin (software version 2.0.3.2)/Galahad Atomic Fluorescence mercury analyzer

9.8 An IBM computer running Millenium software with Windows NT 4.0, service pack 5. The software version may be updated without procedural revision if the new version performs at least as well as the old. The written procedure will be revised if a software update requires procedural modification.

9.9 Printer: Accessed through the laboratory intranet.

9.10 Vials, 40 mL with PTFE-lined caps

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Inspect the waste container bottle on the floor by the instrument before starting analysis. If the bottle is full, dispose of the liquid appropriately.

10.2 Under normal conditions, the PSA trace level mercury analyzer requires very little operational maintenance. However, the preventive maintenance schedule below must be followed to maintain consistent results:

10.2.1 Daily:

10.2.1.1 Before shutdown, flush all tubing and the sample valve with a suitable wash liquid (normally deionized water). Finally, flush with air.

10.2.1.2 For some situations tubing replacement will be necessary. However, flushing of the sample valve must still be done.

10.2.1.3 Replace the pump tubing if worn or in doubt about contamination.

10.2.1.4 Glassware must be clean. If in doubt about contamination, clean the glassware thoroughly.

10.2.1.5 Clean all outer surfaces of the instrument with a damp lint-free cloth.

10.2.1.6 After shutdown, release the pump tubing tension.

10.2.2 Weekly:

10.2.2.1 Perform the daily maintenance.

10.2.2.2 Pump tubing must be replaced, if not replaced as part of daily routine during the week.

10.2.3 Monthly:

10.2.3.1 Perform daily and weekly maintenance.

10.2.3.2 Pump tubing must be replaced, if not replaced any day of the previous week.

10.2.3.3 Check for signs of discoloration in the Perma Pure dryer membrane. Replace when discolored.

10.2.4 Six Months:

10.2.4.1 Perform daily, weekly, and monthly maintenance.

10.2.4.2 Replace the Perma Pure dryer membrane if needed.

10.2.5 Annually:

10.2.5.1 Perform daily, weekly, monthly, and six-month maintenance before samples are analyzed.

10.2.5.2 Replace the Perma Pure dryer membrane if needed.

10.2.5.3 Replace the activated charcoal in the instrument exhaust line.

10.2.6 Cleaning:

10.2.6.1 Before cleaning the instrument, disconnect the main supply cable. Cleaning must ONLY be done on accessible parts of the instrument, such as the outer case.

10.2.6.2 Clean the instrument with a damp lint-free cloth or sponge previously immersed in warm soapy water. Alternatively, a suitable laboratory cleaning fluid may be used. Avoid using copious amounts of liquid when cleaning, as running liquid can reach internal electronics and cause damage. Use only a damp lint-free cloth.

10.2.7 Finish cleaning by wiping all wet surfaces with a dry lint-free cloth or sponge.

10.2.8 Acid Spills: Acid spills on or around the mercury analyzer must be wiped up IMMEDIATELY with a suitable neutralizing agent. Do not allow copious amounts of liquid or neutralizer to contact the instrument as running liquid can reach internal electronics and cause damage.

11.0 CHEMICALS AND REAGENTS

11.1 Concentrated Hydrochloric Acid (HCl) – Trace metal grade or better (must be mercury-free).

11.2 Hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) - Dissolve 6.0 g of NH_2OH-HCl in reagent water and bring to 50 g. This solution must be made daily.

11.3 Stannous Chloride ($SnCl_2 \cdot 2H_2O$) - Dissolve 20 g of $SnCl_2 \cdot 2H_2O$ in 100 mL concentrated HCl. After crystals are dissolved, dilute to 1000 g with reagent water. This solution must be made daily.

11.4 Bromide/Bromate solution (Br^-/BrO_3^-) - Add the contents of one Environmental Express (catalog #HP9010) tube to 90 mL concentrated HCl, in a 125 mL polyethylene bottle. Final concentration is 0.1N. Remake this solution each day that samples are run.

11.5 Reagent water is prepared from city water by running through a carbon filter, reverse osmosis, deionization and a four-bowl Milli Q system. Reagent water resistivity must read at least 18 MΩ-cm before use.

11.6 The argon carrier gas supply must be grade 5.0 or better. This is plumbed from a liquid argon tank located outside the building.

12.0 STANDARDS PREPARATION

12.1 The mercury stock solution is purchased at a concentration of 1000 mg/L from Inorganic Ventures. The second-source calibration verification (SCV) standard solution is purchased at 1000 mg/L from SCP Science. All stock solutions are ICP grade single-element solutions.

12.1.1 Purchased stock standards have an expiration date of one year from the date received unless otherwise specified by the manufacturer.

12.1.2 Input all purchased stock standards to the laboratory information management system (Element™).

12.1.3 Intermediate and working dilutions from purchased stock standards must be replaced daily but do not need input daily if previously documented in the system. If not replaced daily, a dilution needs input to the system under a different standard number.

12.2 Preparation of a 1000 ug/L mercury solution is as follows:

12.2.1 Label a clean 100 mL volumetric flask.

12.2.2 Add about 20 mL of reagent water.

12.2.3 Pipette 100 µL of the 1000 mg/L mercury stock solution into the flask.

12.2.4 Bring the solution to volume with reagent water. Stopper and mix well.

12.3 Preparation of a 1.0 ug/L mercury solution

12.3.1 Label a clean 100 mL volumetric flask.

12.3.2 Add about 20 mL of reagent water.

12.3.3 Pipette 100 µL of 1000 ug/L standard into the flask.

12.3.4 Bring the solution to volume with reagent water. Cap the volumetric and mix well.

12.4 Preparation of working standards

12.4.1 Preparation of a 10 ng/L standard

12.4.1.1 Label a clean 500 mL volumetric flask.

12.4.1.2 Add about 200 mL of reagent water.

12.4.1.3 Pipette 5000 µL of the 1.0 ug/L standard into the flask.

12.4.1.4 Bring the solution to volume with reagent water. Cap the volumetric and mix well.

12.4.1.5 Pour the standard into a clean labeled 40 mL vial.

12.4.2 Preparation of a 5.0 ng/L standard

12.4.2.1 Label a clean 500 mL volumetric flask.

12.4.2.2 Add about 200 mL of reagent water.

12.4.2.3 Pipette 2500 µL of the 1.0 ug/L standard into the flask next.

12.4.2.4 Bring the solution to volume with reagent water. Cap the volumetric and mix well.

12.4.2.5 Pour the standard into a clean labeled 40 mL vial.

12.4.3 Preparation of a 2.0 ng/L standard

12.4.3.1 Label a clean 500 mL volumetric flask.

12.4.3.2 Add about 200 mL of reagent water.

12.4.3.3 Pipette 1000 µL of the 1.0 ug/L standard into the flask.

12.4.3.4 Bring the solution to volume with reagent water. Cap the volumetric and mix well.

12.4.3.5 Pour the standard into a clean labeled 40 mL vial.

12.4.4 Preparation of 1.0 ng/L standard

12.4.4.1 Label a clean 500 mL volumetric flask.

12.4.4.2 Add about 200 mL of reagent water.

12.4.4.3 Pipette 500 µL of the 1.0 ug/L standard into the flask.

12.4.4.4 Bring the solution to volume with reagent water. Cap the volumetric and mix well.

12.4.4.5 Pour the standard into a clean labeled 40 mL vial.

12.4.5 Preparation of 0.5 ng/L standard

12.4.5.1 Label a clean 500 mL volumetric flask.

12.4.5.2 Add about 200 mL of reagent water.

12.4.5.3 Pipette 250 µL of the 1.0 ug/L standard into the flask.

12.4.5.4 Bring the solution to volume with reagent water. Cap the volumetric and mix well.

12.4.5.5 Pour the standard into a clean labeled 40 mL vial.

12.5 Preparation of a Secondary Calibration Verification (SCV)

12.5.1 Preparation of the SCV (1,000 ug/L mercury)

12.5.1.1 Label a clean 100 mL volumetric flask.

12.5.1.2 Add about 20 mL of reagent water.

12.5.1.3 Pipette 100 µL of a second-source stock standard (1000 mg/L) into the flask.

12.5.1.4 Bring the solution to volume with reagent water. Cap the volumetric and mix well.

12.5.2 Preparation of a 1.0 ug/L SCV solution

12.5.2.1 Label a clean volumetric flask.

12.5.2.2 Add about 20 mL of reagent water.

12.5.2.3 Pipette 100 µL of 1000 ug/L SCV solution from Section 12.5.1 into the flask.

12.5.2.4 Bring the solution to volume with reagent water. Cap the volumetric and mix well.

12.5.3 Preparation of a 3.0 ng/L SCV Standard

12.5.3.1 Label a clean 40 mL vial.

12.5.3.2 Fill with reagent water then withdraw 3.7 mL.

15.5.3.3 Pipette 120 µL of the 1.0 ug/L SCV solution from Section 12.5.2 into the flask.

15.5.3.4 Cap and mix well.

13.0 SAMPLE PREPARATION

13.1 All collected samples and matrix spikes must be oxidized with BrCl before analysis according to the following steps, assuming 40 mL of sample. Adjust volumes accordingly for sample volumes that are greater than 40 mL.

13.1.1 Samples can remain unpreserved for up to 28 days from the date of collection if and only if oxidation is performed directly in the sample vial for the total volume collected. Otherwise, samples must be preserved within 48 hours from the time of collection.

13.1.2 To preserve a sample in the original collection vial, withdraw 3.7 mL of sample from the collection vial and discard. This reduces the volume in the vial to an apparent 40.0 mL. If the collection vial is to be a spiked sample, add the spike then add 500 µL of BrCl solution and cap tightly.

13.1.3 After adding BrCl, let the collection vial sit for at least 12 hours, then check for a permanent yellow color. If the yellow color has dissipated, add an additional 500 µL of BrCl. Starch iodide strips can also be used to assure complete oxidation of the sample.

13.1.4 Let the vial sit for at least 12 hours again. Check for a permanent yellow color. If the sample remains yellow after 12 hours, it is preserved for sample analysis, which must be completed within 90 days of the sampling date.

13.1.5 If more BrCl solution is added to a sample than is in the standards, it must also be added to at least one of the method performance blanks in the same analytical batch. Also, adding more BrCl to the collection bottle will necessitate the use of a dilution factor in calculating a final result.

13.1.6 Preparation of extra reagent blank solution for sample dilutions is as follows:

13.1.6.1 Add laboratory reagent water to at least four 40 mL vials.

13.1.6.2 Add 500 µL of BrCl solution and cap tightly.

13.1.6.3 Let the vials sit for at least 12 hours then process with samples needing diluted.

13.2 Fill out an ID/WT sheet for each analytical batch. Each line on the ID/WT sheet represents a discreet autosampler position. If a sample requires a Matrix Spike (MS) and Matrix Spike Duplicate (MSD), three autosampler positions must be used. If a sample is diluted, enter the dilution factor in the column provided.

Note: Continuing Calibration Verification (CCV) solutions do not need placed repeatedly within the analysis sequence. The original CCV autosampler position can be referenced when entering the run sequence program.

13.3 Oxidation of calibration blanks, calibration standards, initial calibration verifications (ICV), continuing calibration verifications (CCV), blanks (BLK) and secondary calibration verifications (SCV) must be done at the same time as samples. Withdraw 3.7 mL from the vial and add 500 µL of 0.1N BrCl solution to each standard, ICV, CCV, BLK and SCV. Cap each vial and mix well.

13.4 Prior to analysis, all calibration blanks, calibration standards, ICV's, CCV's, BLK's, SCV's and samples must have hydroxylamine hydrochloride solution added to stop the digestion. To each calibration blank, standard, BLK, ICV, CCV add 20 µL of hydroxylamine hydrochloride cap and mix well. If more than 500 µL of BrCl was added, pipette an additional 20 µL of hydroxylamine hydrochloride to the sample, and an additional 20 µL to the corresponding BLK. Cap each sample and mix well. A minimum of 5 minutes must elapse before analysis can begin.

13.5 If a sample is to be filtered in the lab. The filtering process must be completed within 48 hours of sample collection. A filter blank must also be completed at the time the samples are filtered.

13.6 If a sample contains large amounts of solids, several dilutions should be performed on the sample within 48 hours of sample collection to ensure reportable data.

14.0 CALIBRATION PROCEDURES

14.1 The average of at least three reagent blanks and five or more non-zero standards comprise the initial calibration. Preparation of these standards is discussed in Section 12.0. The calibration must be prepared with (and in the same manner as) samples. A Continuing Calibration Verification (CCV) is required before and after each analytical batch. The batch may contain up to 20 samples but no more.

14.2 Load the autosampler tray with calibration standards. These standards are loaded starting with Position 11, which contains only reagent water. Position 12 and 13 also contain reagent water. Position 14 contains a 0.5 ng/L mercury standard. Position 15 contains a 1.0 ng/L standard. Position 16 contains a 2.0 ng/L standard. Position 17 contains a 5.0 ng/L standard. Position 18 contains a 10.0 ng/L standard.

14.3 Calibration

14.3.1 A calibration must contain five or more non-zero points and three reagent blanks. The lowest non-zero calibration point must be at the reporting limit.

14.3.2 The Millennium software calculates a calibration factor (CF) for each calibration point as follows:

$$CF = \frac{H_C - H_{avg\ blank}}{C}$$

Where:

H_C = Calibration point peak height
$H_{avg\ blank}$ = Average reagent blank peak height
C = Calibration point concentration, in ng/L

14.3.4 If RSD is less than or equal to 15%, verify that the lowest calibration standard recovery is 75 – 125% of the expected value. If both criteria are acceptable, the average calibration factor is acceptable for sample analysis. If RSD is greater than 15% or the lowest calibration standard recovery exceeds 75 – 125%, repeat the calibration and calibration checks once. If the calibration remains unacceptable, locate and correct the problem before re-calibrating and/or sample analysis.

15.0 ANALYTICAL PROCEDURE

15.1 This procedure assumes the user has been introduced to the software by reading the manual or by training with experienced analysts.

15.2 Make sure the argon supply is on. There is a wall valve leading from the source to the left of the instrument that must be opened. Set the argon pressure to 30 psi.

15.3 Check all peristaltic tubing. If any tubing is cracked or badly worn, replace it. When clamping the tubing, make sure the tubing is lined up with the pump rollers.

15.4 Calibrate in accordance with the manufacture's instructions.

15.4.1 The software will automatically subtract the average of three calibration blanks each standard when calculating CF_{avg}, RSD and lowest standard recovery. A prompt will appear if any criterion is unacceptable that automatically stops the calibration sequence.

15.4.2 If the calibration sequence has been stopped due to unacceptable RSD and/or low standard recovery, locate and correct the problem then repeat the calibration sequence.

15.5 Verify the instrument method used is "TriMatrix 1631E" and the following settings.

15.5.1 Be sure "mercury" is entered in the element window.

15.5.2 The detector setting (1, 10, 100 or 1000) will depend on the reporting limit required.

15.5.3 The filter must be set to 32.

15.5.4 Autozero must be checked.

15.5.5 The mode must be "ratio".

15.5.6 Select "fill filter before plot".

15.5.7 Verify both pump speeds. Pump 1 must be at full and pump 2 must be ½ speed.

15.5.8 Verify all Analysis Sequence Settings.

15.5.8.1 Delay must be set at 20.

15.5.8.2 Analysis must be set at 60.

15.5.8.3 Valve Flush must be checked.

15.5.9 Verify all Galahad sequence settings:

15.5.9.1 Delay must be set to 20.

15.5.9.2 Heat must be set to 15.

15.5.9.3 Cool must be set to 60.

15.6 Check the peristaltic tubing to ensure that all pumps are drawing liquid. Lift the sample line out of the rinse solution to see if the pump pulls air. Check the stannous chloride line, the same way. Check the blank line the same way. If any lines are not drawing liquid, increase the tension. If this does not work, try changing the tubing. If this does not work, a plug must be suspected and close inspection of the sample introduction system is required for corrective action.

15.7 Enter the calibration and sample information into the computer and run the sequence:

15.7.1 Calibration standards will be analyzed and the new calibration will be displayed.

15.7.2 Verify the calibration as acceptable in accordance with Section 14.0 criteria.

15.7.3 If the calibration fails, rerun any point from the curve that is obviously suspect or perform any necessary corrective action on the system and recalibrate entirely.

15.7.3.1 Replacing a calibration point without an obvious suspicion the point is abnormal is not a substitute for corrective action for unacceptable calibration solutions. If more than one data point appears suspect, the entire calibration series must be remade.

15.7.3.2 Deleting a calibration point without an obvious suspicion the point is abnormal, is not a substitute for corrective action of unacceptable calibration solutions. If more than one data point appears suspect, the entire calibration series must be remade.

15.8 After calibration, a 5.0 ng/L mercury initial calibration verification (ICV) must be run. The ICV recovery must be within 77 – 123% of the expected value. If ICV recovery is not 77 – 123%, the run must be stopped and the following steps taken:

15.8.1 Re-analyze the ICV one time.

15.8.2 If the ICV fails again, implement corrective action. Corrective action may include gas flow adjustment, replacing tubing or other mechanical details. After the problem has been corrected, repeat the calibration.

15.9 Once all initial quality control passes samples may be analyzed. An analytical batch consists of at least three method performance blanks (BLK) which are reagent blanks, a second-source calibration verification (SCV) which is a second source standard and up to 20 samples.

15.10 A continuing calibration verification (CCV) must be analyzed at the end of each analytical batch.

15.10.1 A CCV is the 5.0 ng/L calibration standard analyzed as a sample. Percent recovery for the CCV must be within 77 – 123% of the expected value.

15.10.2 If a CCV result does not fall within the control limits, re-analyze the CCV one time.

15.10.3 If the second CCV result fails, the run must be stopped. Correct the problem and re-analyze all samples since the last acceptable CCV. If a CCV cannot be recovered within the control limits, return to Section 15.9.5.

15.11 Inspect the raw data to make sure all results are within the calibration range. Dilute and re-analyze any result above the calibration range. Samples must be diluted using reagent blank solution (Section 13.1.6).

16.0 CALCULATIONS AND DATA HANDLING

16.1 Calculate samples without additional BrCl solution added using the following equation:

$$\text{Hg (ng/L)} = \frac{(H_{sample} - H_{avg\ blank})}{CF_{avg}}$$

Where:

H_{sample} = Peak height for Hg in the sample
$H_{avg\ Blank}$ = Average peak height for Hg in the blank
CF_{avg} = Average calibration factor (Section 14.4.2)

16.2 Calculate samples WITH additional BrCl solution added using the following equation:

$$\text{Hg (ng/L)} = \frac{(H_{sample} - H_{avg\ blank})}{CF_{avg}} \left| \frac{(V_{std} - V_{reagent\ in\ std})}{(V_{sample} - V_{reagent\ in\ sample})} \right.$$

Where:

H_{sample} = Peak height for Hg in the sample
$H_{avg\ Blank}$ = Average peak height for Hg in the blank
CF_{avg} = Average calibration factor (Section 14.4.2)
V_{std} = Volume used for standards, in mL
$V_{reagent\ in\ std}$ = Volume of reagents used in the calibration standards, in mL

V_{sample} = Volume of sample used, in mL
$V_{reagent\ in\ sample}$) = Volume of reagents used in the sample, in mL

16.3 Refer to Attachment 23.3 for an analysis sequence report example.

17.0 DATA REPORTING AND DELIVERABLES

17.1 Analysts running samples are responsible for correctly filling in, handing in and filing all associated analytical paperwork. It is essential to perform these tasks consistently to provide the best possible laboratory and client defensible data.

17.2 After analysis, data is uploaded to the laboratory information management system (Element™) in accordance with TriMatrix SOP GR-10-123.

17.3 If an internal chain-of-custody (COC) is required, it is very important that COC forms be filled in correctly and returned to the COC file location.

17.4 Paperwork is handled as follows:

17.4.1 Instrument run logbooks and maintenance logbooks must be filled in completely and correctly.

17.4.2 All corrections are to be made with indelible ink.

17.4.3 **Corrections must be made with a single lineout, which is then dated and initialed. Write-overs are NOT acceptable.** Erroneous results must remain legible. Place any new result near the incorrect result.

17.4.4 Mark out blank areas in a logbook with a "Z".

18.0 QUALITY ASSURANCE

18.1 All quality control data must be maintained and available for easy reference and inspection. In addition to the quality control parameters already discussed, the following QC requirements apply.

18.1.1 Cleaning

18.1.1.1 New bottles and vials are cleaned by rinsing with reagent water and filling with 0.4% HCl. The filled bottles and vials are placed in two Ziploc bags, and finally stored inside a plastic container until use.

18.1.1.2 A set of 24 bottles or 72 vials must be cleaned at one time and given a unique batch number. Before being sent to the field for sample collection, two bottles from the batch must be tested to ensure the batch is mercury-free at the reporting limit. The first bottle in every batch must be tested, and a random bottle from 11-

24 must be tested. If mercury above 0.5 ng/L is observed in either bottle, the entire batch must be rejected and cannot be used.

18.1.1.3 Each bottle in a batch must have a label identifying the batch it came from and a number from 1-24 placed on it. This allows the lab to track each bottle. Each vial in a batch must have a label identifying the batch it came from and a number from 1-72 placed on it.

18.2 Calibration standards must be prepared daily, with a minimum of five non-zero standards and three blanks.

18.3 Dilute and re-analyze all samples with concentrations greater than the highest standard in the calibration range. Samples must be diluted with reagent blank solution (Section 13.1.6).

18.4 Include a minimum of three method blanks, and one SCV per sample batch of up to 20 samples.

18.4.1 An SCV is a second-source standard purchased from a different vendor than the one used to prepare calibration standards. Refer to Section 12.5 for the SCV preparation.

18.4.1.1 Calculate SCV percent recovery using the following equation:

$$Percent\ Recovery = \frac{C_{Spike}}{Spike\ Quantity} x\,100$$

18.4.1.2 The SCV percent recovery must be within established historical limits of the expected value.

18.5 Matrix Spikes (MS) and Matrix Spike Duplicates (MSD) are samples spiked with a known concentration of mercury. Analyze one MS and one MSD at a frequency of at least 1 spike to every 10 samples. The MS documents whether there is a matrix effect on sample preparation. The MSD documents precision within a matrix.

18.5.1 Withdraw 3.7 mL of sample from the extra two vials collected. Pipette 100 µL of the 1000 ng/L standard prepared in Section 12.3. The diluted concentration is 2.5 ng/L mercury. Preserve the spiked samples as discussed in Section 13.

18.5.2 Calculate spike recovery using the following equation:

$$Percent\ Recovery = \frac{C_{Spike} - C_{Orig}}{Spike\ Quantity} x\,100$$

Where:
C_{Spike} = The spiked sample result calculated from the calibration, in ng/L
C_{Orig} = The unspiked sample result, in ng/L
Spike Quantity = The mercury spike concentration, in the sample, in ng/L

18.5.3 Calculate precision between duplicate spikes using the following equation:

$$Relative\ Percent\ Difference = \frac{|C_{MSD} - C_{MS}|}{\frac{C_{MSD} + C_{MS}}{2}}$$

Where:
C_{MSD} = MSD concentration, in ng/L
C_{MS} = MS concentration, in ng/L

18.5.4 The MS/MSD must recover within 71-125% of the expected value.

18.5.5 Relative percent difference between the MS and MSD must be ≤24%.

18.6 Check the calibration by analyzing appropriate quality control check standards as follows:

NOTE: Steps 18.6.2 through 18.6.4 must be performed every time the instrument is calibrated.

18.6.1 Calibrate the instrument using at least five standards and the mean of at least three blanks.

18.6.2 Initial Calibration Verification (ICV) is analyzed after the calibration. Percent recovery limits are 77% to 123% of the expected value. If percent recovery is not within acceptance limits, correct the problem, re-calibrate if necessary, and restart the analysis.

18.6.3 At the end of each run, verify the calibration.

18.6.3.1 A Continuing Calibration Verification (CCV) is analyzed after the last sample in the run.

18.6.3.2 Percent recovery limits are 77 to 123% of the expected value. If percent recovery is not within acceptance limits, correct the problem. Once the problem is corrected, analyze a CCV.

18.6.3.3 If the CCV is within control limits, restart the analysis from the last good CCV. If the CCV is not within the control limits, repeat Sections 18.6.1 through 18.7.3 and re-analyze all samples since the last good CCV.

18.7 All samples oxidized at the same time must be run within 12 hours of the calibration.

19.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

19.1 Before actual sample analysis, each analyst must demonstrate an ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC). While IDCs are not instrument dependent, one is required on each instrument used for sample analysis to demonstrate the instrument's ability to generate acceptable accuracy and precision as well. Annually, a Continuing Demonstration of Capability (CDC) is required.

19.1.1 Initial Demonstration of Capability

19.1.1.1 Spike four 40 mL aliquots of reagent water so the resulting concentration is 5.0 ng/L. Alternatively, the last four of the seven results used in an MDL study may be used as an IDC if run exclusively by the analyst. ONLY the last four of the seven may be used. Otherwise, process the four spiked waters following every step outlined in the procedure for sample preparation and analysis. Calculate the average percent recovery and standard deviation of the average. Average percent recovery must be between 79 – 121%. Relative standard deviation of the average must be ≤21%.

19.2 If either criterion is not met, locate and correct the source of the problem and repeat the study. Repeated failure however, will confirm a general problem with the procedure or technique used. If this occurs, locate the source of the problem, correct the procedure or technique used, and repeat the study. Samples may not be analyzed by any analyst or on any instrument until a demonstration of capability study has been successfully completed. Copies of a successful demonstration of capability spreadsheets and raw data must be given to the Quality Assurance department.

19.3 Method Detection Limit Studies

19.3.1 A Method Detection Limit (MDL) study must be performed annually on every instrument using this procedure. Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. Actual reporting limits are derived from MDL studies. The minimum possible reporting limit is equal to the amount spiked in the MDL study, provided the MDL passes. The reporting limit actually achieved with any given sample will vary depending on instrument sensitivity, matrix effects, and dilutions.

19.3.2 The procedure followed for MDL studies is based on the method given in 40 Code of Federal Regulations, Part 136, Appendix B, latest revision.

19.3.3 For sample analysis, the minimum reporting limit is the same concentration as the low point of the calibration curve.

19.3.4 Seven replicate analyses are performed using reagent water at the estimated minimum reportable concentration. The last four of the seven water replicates can also be used for an IDC or CDC, as described in Section 19.1.2.

19.3.5 An average blank measurement is required to calculate the measured level of mercury. Seven separate sets of triplicate blanks must be analyzed, one after each of the seven MDL samples. The average triplicate blank measurement must be subtracted from all seven MDL analyses.

19.3.6 The standard deviation of the average found (blank-subtracted) for mercury using all seven analyses is calculated and multiplied by 3.143. The resulting number is the calculated MDL.

19.3.7 If the concentration spiked is between the calculated MDL and ≤5 times the calculated MDL, and there are no zero percent recoveries in the set of seven, the MDL study passes. If not, the MDL study must be repeated. If a study needs re-analyzed at a different concentration, the entire set of seven needs repeated. If a study fails due to abnormal reproducibility on one value, then that value alone needs repeated. No more than one result in a study can be rejected however. The entire study does not need analyzed in the same analytical batch.

19.3.8 If at any time a reporting limit is above a client or state-desired reporting limit, the calculated MDL value may be used for a reporting limit, provided all results are narrated. The narration must state that the reporting limit is based on a calculated MDL value and mercury when spiked at that level, was not observed.

20.0 POLLUTION PREVENTION

20.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

20.2 Never dispose of laboratory chemicals without first referencing appropriate written instructions of disposal for that particular material.

20.3 Conserve the use of chemicals where applicable.

20.4 Comply with all environmental laws associated with chemicals in the laboratory.

21.0 WASTE MANAGEMENT

21.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals.

21.2 To minimize the environmental impact and costs associated with the disposal of chemicals, order and use only the minimum amount of material required.

21.3 Follow all instructions in TriMatrix SOP GR-15-102 (Laboratory Waste Disposal) for laboratory waste disposal.

22.0 REFERENCES

22.1 *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry,* Method 1631, Revision E: August 2002, USEPA, Office of Water Publication, EPA-821-R-02-019

23.0 ATTACHMENTS

23.1 Standards Record Example

23.2 Preparation Batch Report Example

23.3 Analysis Sequence Report Example

Attachment 23.1
Standards Record Example

Analytical Standard Record

TriMatrix Laboratories, Inc.

7100210

Description:	Mercury 1000 mg/L for SCV	Expires:	May-31-09
Standard Type:	Calibration Star	Prepared:	May-31-07
Solvent:	2% HNO3	Prepared By:	** Vendor **
Final Volume (mls):	1	Department:	Expired
Vials:	1	Last Edit:	Dec-18-07 15:10 by DSC

Environmental Express part# HP100033-1
Lot: 0717029
Received 10/5/07

Analyte	CAS Number	Concentration	Units
Mercury, OWEP-TAR	7439-97-6	1000	ug/mL
Mercury, OWEP-SAR	7439-97-6	1000	ug/mL
Mercury	7439-97-6	1000	ug/mL

Approved By: 1-8-09
QA Officer

Approved By: DK 1-19-09
Area Supervisor

Attachment 23.2
Preparation Batch Report Example

TriMatrix Laboratories, Inc.

PREPARATION BATCH 0703716 Page 1 of 1

Metals, Waste Water, 1631E Digestion

Printed: 4/21/2008 4:37:52PM

Batch comments:
KBr added at 2000 on 4-09-07.
Samples still yellow at 1500 on 4-10-07.

Lab Number	Container	Prepared	By	Initial (mL)	Final (mL)	Client: Source ID	Client: Spike ID	Client: uL Spike	Comments	
0703716-BLK1		Apr-09-07 20:00	DWJ	40	40					
0703716-BLK2		Apr-09-07 20:00	DWJ	40	40					
0703716-BLK3		Apr-09-07 20:00	DWJ	40	40					
0703716-BS1		Apr-09-07 20:00	DWJ	40	40		6120459	60		
0704022-01 *Hg Total 1631E*	A	Apr-09-07 20:00	DWJ	40	40	[redacted]			limit is 30	limit is 30
0704044-01 *Hg Total 1631E*	B	Apr-09-07 20:00	DWJ	40	40	[redacted]				
0704044-02 *Hg Total 1631E*	B	Apr-09-07 20:00	DWJ	40	40	[redacted]				
0704044-03 *Hg Total 1631E*	B	Apr-09-07 20:00	DWJ	40	40	[redacted]				
0704044-04 *Hg Total 1631E*	C	Apr-09-07 20:00	DWJ	40	40	[redacted]				
0704044-05 *Hg Total 1631E*	B	Apr-09-07 20:00	DWJ	40	40	[redacted]				
0704044-06 *Hg Total 1631E*	B	Apr-09-07 20:00	DWJ	40	40	[redacted]				
0704044-07 *Hg Total 1631E*	B	Apr-09-07 20:00	DWJ	40	40	[redacted]				

Comments:	Analyst Initials:

bch_TM_byAnalysis.rpt

Approved By: PJ 1-8-09
QA Officer

Approved By: DSC 1-9-9
Area Supervisor

Attachment 23.3
Analysis Sequence Report Example

TriMatrix Laboratories, Inc. ANALYSIS SEQUENCE 7041075 Page 1 of 1 Printed: 6/29/2007 1:43:24PM

Metals, Waste Water, Apr-10-07

Instrument = 202, Calibration = UNASSIGNED

Sequence Analyses:
Hg Total 1631E

Lab Number	*Analysis*	*Contain*	*STD ID*	*ISTD ID*	*Client / QC Type*	*Extraction Comments*
7041075-ICV1	QC		7030400		INITIAL CAL CHECK	
7041075-SCV1	QC		7040440		SECONDARY CAL CHECK	
0703716-BS1	QC				LCS	
0703716-BLK1	QC				BLANK	
0704022-01	Hg Total 1631E	A 01			[redacted]	limit is 30
0703716-BLK2	QC				BLANK	
0704044-01	Hg Total 1631E	B 01			[redacted]	
0704044-02	Hg Total 1631E	B 01			[redacted]	
0704044-03	Hg Total 1631E	B 01			[redacted]	
0704044-04	Hg Total 1631E	C 01			[redacted]	
0704044-05	Hg Total 1631E	B 01			[redacted]	
0704044-06	Hg Total 1631E	B 01			[redacted]	
0704044-07	Hg Total 1631E	B 01			[redacted]	
0703716-BLK3	QC				BLANK	
7041075-CCV1	QC		7030400		CALIBRATION CHECK	

Comments:	Analyst Initials:

seq_TriMatrix.rpt

Approved By: [signature] 1-8-09
QA Officer

Approved By: DSC 1-19-09
Area Supervisor

TriMatrix Laboratories, Inc.

UNCONTROLLED COPY

STANDARD OPERATING PROCEDURE

Block digestion of Solids for ICP and ICPMS

SW-846 Method 3050B

APPROVALS:

Area Supervisor: Marge A. Scott Date: 01-15-09
Marge A. Scott

QA Officer: Date: 1/15-09
Tom C. Boocher

Operations Manager: Date: 1/15/09
Jeff P. Glaser

Procedure Number: GR-01-137
Revision Number: 1.5

Date Initiated: 2/06/01
Effective Date: 2/1/09

Date Revised: 1/15/09
Pages Revised: All

By: Marge A. Scott

Total Number of Pages: 18

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

1.0 SCOPE AND APPLICATION

1.1 This procedure is applicable to the block digestion of metals in sediment, sludge, soil and RCRA waste for ICP and ICP-MS analysis.

1.2 As the digestion does not attack silicate-bound metals, the procedure is not a total digestion technique for many samples.

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 2, December 1996, Method 3050B, "Acid Digestion of Sediments, Sludge and Soils"

2.1.1 This procedure uses a 50 mL non-constricted block digestion cup as a deviation from method 3050B, which specifies a 250 mL block digestion vessel.

2.1.2 This procedure describes the use of 0.5 g dry weight as a deviation from method 3050B, which specifies the use of 1.0 g dry weight for digestion. However, acid ratios are maintained.

2.1.3 This procedure describes a routine use of the extra digestion step for antimony, tin, silicon and sometimes silver as a deviation from method 3050B, which specifies an optional digestion step for improved antimony, silver, barium and lead recovery.

3.0 SUMMARY OF PROCEDURE

3.1 Homogeneous and dried sediment, sludge and soil sample is weighed directly into a block digestion cup.

3.2 Samples are then digested with repeated additions of nitric acid then hydrogen peroxide.

3.3 If digesting for ICP, hydrochloric acid is used. If digesting for ICPMS, hydrochloric acid is not used.

3.4 All digestates are filtered then brought to a final volume of 50 mL.

3.5 Antimony, tin, silicon and sometimes silver are digested as follows:

3.5.1 Homogeneous and dried sediment, sludge and soil sample is weighed directly into a block digestion cup.

3.5.2 Samples are then digested with nitric acid and hydrochloric acid.

3.5.3 All digestates are filtered then the residue is washed with hot hydrochloric acid and hot laboratory reagent water to increase recovery.

4.0 PARAMETER OR COMPOUND LIST

4.1 This procedure includes digestion for the following elements and instrumental techniques:

ICP	
Aluminum	Silicon
Calcium	Sodium
Iron	Strontium
Lithium	Titanium
Magnesium	
Potassium	

ICP or ICPMS			
Antimony	Chromium	Nickel	Zinc
Arsenic	Cobalt	Selenium	Gold
Barium	Copper	Silver	
Beryllium	Lead	Thallium	
Boron	Manganese	Tin	
Cadmium	Molybdenum	Vanadium	

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal*, latest revision

5.2 TriMatrix SOP GR-01-100, *Inductively Coupled Plasma Atomic Emission Spectrometry using Perkin Elmer Optima 3000/3300DV*, latest revision

5.3 TriMatrix SOP GR-01-129, *Inductively Coupled Plasma-Mass Spectrometry Perkin Elmer ELAN-6000/6100*, latest revision

5.4 TriMatrix SOP GR-10-106, *Inorganic and Metals Laboratories Corrective Actions*, latest revision

5.5 TriMatrix SOP GR-01-115, *Mixing, Grinding and Drying Soils for Metals Analysis*, latest revision

5.6 TriMatrix SOP GR-10-113, *Laboratory Balance Calibration and Verification*, latest revision

5.7 TriMatrix SOP GR-10-111, *Micropipette/Macropipette Calibration and Verification*, latest revision

5.8 TriMatrix SOP GR-16-103, *Glassware Cleaning and Preparation for Wet Chemistry and Metals Laboratories*, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Refer to TriMatrix SOP GR-01-100 for a list of interferences and associated corrective actions when digesting for ICP analysis.

6.2 Refer to TriMatrix SOP GR-01-129 for a list of interferences and associated corrective actions when digesting for ICPMS analysis.

6.3 Some sludge matrices may not be applicable to this procedure.

7.0 SAFETY PRECAUTIONS

7.1 Comply with all instructions for health and safety as outlined in the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan.

7.2 Hot concentrated acids are used in standard and sample preparations. Wear disposable gloves, laboratory coats and approved safety glasses at all times when digesting samples and/or working in the laboratory.

7.3 Refer to the Material Safety Data Sheet (MSDS) library for specific information on any chemical used in the laboratory.

7.4 Check fume hoods to be sure each is functioning properly. All digestions must be done in a fume hood. If the hood is not working properly, immediately contact the area supervisor. Under no circumstances is any block digestion to be performed if the exhaust hood is not on and/or functioning properly.

7.5 Many chemicals and elements used are toxic. Minimize exposure by appropriate use of the personal protective equipment provided.

7.6 No food or drink is allowed in the digestion laboratory at any time, including gum.

7.7 Wash hands before starting work. Substances on the skin may interfere with metals analysis. Wash hands after finishing work. Chemical residuals can be injested and/or carried out of the laboratory if not removed.

7.8 Before leaving the digestion laboratory, remove disposable gloves and laboratory coat. Chemical and/or acid residue transport outside the digestions laboratory needs to be kept to a minimum.

7.9 Rinse all micropipette tips and beakers before disposal or cleaning.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Samples are typically received by the laboratory in 500 mL sample jars.

8.2 Dry at least 30 g of solid sample for analysis and quality control in accordance with TriMatrix SOP GR-01-115. Dry a larger sample aliquot to obtain at least 30 g for low-solids sludge.

8.3 The maximum holding time for all preserved samples requiring this digestion is 180 days.

8.4 Digestates (solubilized samples) ready for analysis need not be refrigerated.

9.0 INSTRUMENTATION, APPARATUS AND MATERIALS

9.1 Micropipette, capable of delivering 250 µL

9.2 Block digester for metals digestion, Environmental Express, HotBlock™, model SC154

9.3 Block digestion cups, 50 mL, certified pre-cleaned and calibrated, Environmental Express, catalog SC475

9.4 Ribbed watchglass, disposable, Environmental Express, catalog SC505

9.5 Filtermate™, Environmental Express, catalog SC0501, for digestate filtration

9.6 Non-ribbed watchglass, disposable, SCP Science, catalog 010-500-081

9.7 Thermometers, NIST-traceable, digital, capable of reading to at least 100° C in 0.1° C increments.

9.8 Analytical balance, capable of weighing to 0.0001 g

9.9 Filter paper, Whatman no. 41 or equivalent

9.10 PTFE sieve, USS #10

9.11 Volumetric flask, 50 mL, type A

9.12 Filter funnels

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Verify and document micropipette calibration in accordance with TriMatrix SOP GR-10-111.

10.2 Clean the block digester and counters daily or if a spill occurs.

10.3 Calibrate the analytical balance in accordance with TriMatrix SOP GR-10-113.

11.0 CHEMICALS AND REAGENTS

11.1 Laboratory reagent water (ASTM Type II), MilliQ water system

11.2 Nitric acid (HNO_3), concentrated, trace metal grade

11.3 Prepare 1:1 (v/v) HNO_3 as follows:

11.3.1 Carefully measure 50 mL of HNO_3 to 50 mL of laboratory reagent water.

11.3.2 Prepare fresh daily.

11.4 Prepare 5% (v/v) HNO_3 as follows:

11.4.1 Carefully measure 5 mL of HNO_3 to 95 mL of laboratory reagent water.

11.4.2 Prepare fresh daily.

11.5 Hydrochloric acid (HCl), concentrated, trace metal grade

11.6 Hydrogen peroxide (H_2O_2), 30%, ACS grade

12.0 STANDARDS PREPARATION

12.1 Multi-element spiking solutions are purchased as commercially prepared solutions.

12.2 Refer to Attachments 20.1 and 20.2 for ICP spiking solution examples.

12.3 Refer to Attachments 20.3 and 20.4 for ICPMS spiking solution examples.

13.0 ANALYTICAL PROCEDURE

13.1 Sediment, soil and sludge digestion is as follows:

13.1.1 Preheat the block digester and adjust the temperature so 50 mL of 5% (v/v) nitric acid is maintained at 85° C. The addition of a watchglass at 85° C adds 10 degrees and maintains the digestion at 95° ±5° C while refluxing.

13.1.2 Mix and/or grind dried sample thoroughly, passing through a USS #10 sieve if necessary. For each sample, transfer 0.5 ±0.0005 g to a block digester cup. For best results, weigh sample directly into a tared digester cup at the balance. Record the actual mass used.

13.1.3 For all digestions, add 5.0 mL of 1:1 (v/v) HNO_3. Cover with a non-ribbed watchglass and reflux in the block digester at 95° ±5° C for 15 minutes. Do not boil.

13.1.4 After 15 minutes, remove from the digester to cool then measure 2.5 mL concentrated HNO_3 into each cup and cover with a non-ribbed watchglass. Reflux for 30 minutes. Repeat this step by adding 2.5 mL acid volumes and refluxing until brown fumes are no longer given off. Brown fumes indicate the digestion is not yet complete.

13.1.5 Once digestion is complete, change to a ribbed watchglass and evaporate to approximately 2.5 mL. Do not boil or let any part of the digestion cup bottom go dry. Repeat any sample digestion in which the digestion cup goes dry. Boiling should not occur if the block digester is properly adjusted.

13.1.6 When the volume is approximately 2.5 mL, remove and cool to room temperature. It is very important to have digestates at room temperature to avoid splattering when adding hydrogen peroxide. Add 1.0 mL of laboratory reagent water and 1.5 mL of 30% H_2O_2 slowly. Let any initial reaction occur without heat.

13.1.7 Reduce the block temperature by 10° C to control excess effervescence while still maintaining enough heat to maintain the peroxide reaction. Cover with a non-ribbed watchglass and return to the block digester, heating until any reaction stops. If effervescence becomes so vigorous that splattering is immanent, control by lifting from the heat until it subsides. Do not let digestate overflow the digestion cup as analyte will be lost. Repeat the digestion if overflow occurs.

13.1.8 For samples that continue to react, carefully add another 1.0 mL of 30% H_2O_2. Do not add more than a total of 5.0 mL. Repeat until no further reaction occurs or until the maximum 5.0 mL volume has been added.

13.1.9 After the H_2O_2 digestion is complete, cover with a ribbed watchglass and again evaporate to 2.5 mL. Do not boil or let the bottom of any digestion cup go dry.

13.1.10 After reducing the volume, remove from the heat and cool to room temperature again. For ICP sample analysis only, add 5.0 mL of concentrated HCl. Cover with a non-ribbed watchglass and reflux at 95° ±5° C for 15 minutes. Skip this step if the digestion is for ICPMS analysis.

13.1.11 Cool to room temperature, dilute to 50 mL with laboratory reagent water then use a Filtermate™ for removing particulates.

13.1.11.1 Perform the filtration slowly with little pressure placed to the plunger.

13.1.11.2 If excessive backpressure occurs, stop filtering and let the digestate settle out before continuing. Applying too much pressure to the Filtermate™ plunger can cause the filter to fail allowing particulates into the filtrate.

13.1.11.3 Do not rinse the filter since the final volume has already been measured.

13.1.12 Samples are ready for analysis after filtering.

13.2 Sediment, soil and sludge digestion for antimony, tin, silicon and sometimes silver is as follows:

13.2.1 Preheat the block digester and adjust the temperature so 50 mL of 5% (v/v) nitric acid is maintained at 85° C. The addition of a watchglass at 85° C adds 10 degrees and maintains the digestion at 95° ±5° C while refluxing.

13.2.2 Mix and/or grind dried sample thoroughly, passing through a USS #10 sieve if necessary. For each sample, transfer 0.5 ±0.0005 g to a block digester cup. For best results, weigh sample directly into a tared digester cup at the balance. Record the actual mass used.

13.2.3 Add 1.25 mL concentrated HNO_3 and 5.0 mL concentrated HCl. Cover with a non-ribbed watchglass and heat at 95 ±5° C for 15 minutes. Do not boil.

13.2.4 After 15 minutes, filter through Whatman no. 41 filter paper, collecting the filtrate in a 50 mL volumetric flask. Wash the filter paper while still in the filter funnel with no more than 2.5 mL of hot (~95° C) concentrated HCl then with 10 mL of hot ASTM Type II water. Collect all washings in the same 50 mL volumetric flask.

13.2.4 Return the filter and residue to the digestion cup. Add 2.5 mL of hot (~95° C) concentrated HCl. Return to the block digester with a non-ribbed watchglass and heat at 95 ±5° C until the filter paper dissolves. Remove from the digester. Rinse the watchglass and digestion cup sides with laboratory reagent water. Filter again and collect the filtrate in the same 50 mL volumetric flask. Let the filtrate cool to room temperature in the flask then dilute to volume with laboratory reagent water.

13.2.5 High concentrations of metal salts may precipitate upon cooling. If precipitation occurs, do not dilute to volume. Instead, add up to 5.0 mL of concentrated HCl to dissolve the precipitate. After the precipitate dissolves, dilute to volume.

13.2.6 After diluting, digestates are ready for analysis by ICP.

14.0 DATA REPORTING AND DELIVERABLES

14.1 Work orders are printed out by the Laboratory Information Management System (Element™) indicating which samples need digestion.

14.1.1 Initial and date any hand-written information on the work order report.

14.1.2 Organize and archive all work order forms in accordance with the TriMatrix quality assurance manual.

14.2 Completion of each sample with all quality control is entered back into Element™ and a preparation batch report is printed.

14.2.1 Enter all information associated with the digestion before printing.

14.2.2 The preparation batch report accompanies the sample digestion batch to the instrumental laboratory.

14.2.3 Initial and date any hand-written information on the preparation batch report.

14.2.4 Organize and archive all preparation batch report forms in accordance with the TriMatrix quality assurance manual.

14.3 Maintain the use of all standards and reagents in Element™ for traceability. Certificates of analysis are maintained on the laboratory intranet library for each standard and reagent used.

14.4 Analysts preparing digestion batches are responsible for correctly filling in, transferring and filing all associated paperwork. This is essential in providing the client with defensible data.

14.5 If internal chain-of-custody (CoC) is required, it is very important that CoC forms be filled in completely and correctly. Organize, transfer and/or archive CoC forms in accordance with the TrMatrix quality control manual.

14.6 Fill in block digester maintenance logbooks completely and correctly when maintenance is performed. Indicate blank areas in logbooks with a large "Z" that is dated and initialed.

14.7 Make corrections in any logbook or on any hardcopy with a single line over the mistake (not a writeover or scribble) then date and initial any new writing.

14.8 Silicon digested by this procedure must be reported and/or narrated as being "recoverable silicon" since most soil silicates are not digested by the acids used.

15.0 QUALITY ASSURANCE

15.1 At least one digestion blank (BLK) must be carried through the entire digestion to monitor contamination with each digestion batch of up to 20 samples. Prepare the blank by digesting an empty digestion cup as a sample and using the maximum acid additions and digestion steps used in the digestion batch.

15.2 At least one blank spike (BS) must be carried through the entire digestion to document recovery without matrix interference in each digestion batch of up to 20 samples. Prepare blank spikes as follows:

15.2.1 For ICP digestions, measure 5.0 mL 1:1 (v/v) HNO_3 into a digestion cup and spike with 250 uL each of standards SSW-1A and SSW-SSS-2A. Perform the digestion using the maximum acid additions and digestion steps used in the sample batch.

15.2.2 For ICPMS digestions, measure 5.0 mL 1:1 (v/v) HNO_3 into a digestion cup and spike with 100 uL each of standards HP solutions A and B. Perform the digestion using the maximum acid additions and digestion steps used in the sample batch.

15.3 At least one matrix spike (MS)/matrix spike duplicate (MSD) must be prepared for each digestion batch of up to 20 samples to monitor matrix recovery and precision. Perform a MS/MSD for each matrix being digested (sediment, soil, sludge or unknown).

15.3.1 For ICP matrix spikes, measure 0.5 g of dried sample into a digestion cup and spike with 250 uL each of standards SSW-1A and SSW-SSS-2A. Perform the digestion using the same acid additions and digestion steps used in the un-spiked sample.

15.3.2 For ICPMS matrix spikes, measure 0.5 g of dried sample into a digestion cup and spike with 100 uL each of standards HP solutions A and B. Perform the digestion using the same acid additions and digestion steps used in the un-spiked sample.

15.4 Digestates must not boil during the evaporation step. If a digestate begins to boil during evaporation, immediately remove from the block and reduce the temperature. Some boiling will be evident during the reflux step. However, vigorous boiling during reflux will diminish the water-acid azeotrope and cause loss of analyte. If a digestate begin to boils vigorously during refluxing, immediately remove from the block and reduce the temperature. If boiling during evaporation or vigorous boiling during refluxing is not immediately addressed, discard and the re-prepare the sample and/or samples affected. Monitor the block temperature closely to minimize re-preparation.

15.5 Each commercially purchased spiking solution must be used within its expiration date. If a standard or solution has expired, remove it from the laboratory for proper disposal.

15.6 If a sample evaporates to dryness, some metals will be volatilized. If any portion of the digestion cup bottom goes dry, discard the digestate and re-prepare the sample in another batch.

16.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

16.1 Before processing actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC). Analysts responsible for sample processing by this procedure must pass an IDC study first.

16.1.1 Initial Demonstration of Capability Study

16.1.1.1 Spike four digestion cups as in a blank spike preparation. Digest the four spikes following every step in this procedure and obtain analysis results for the four blank spikes. Analysis of the spikes must also include every step in the analytical procedure. Enter all four results obtained into the IDC spreadsheet located on the laboratory intranet library to calculate average percent recovery and relative standard deviation. Average recovery must fall within the blank spike control limits found in Element™. Relative standard deviation must be less than or equal to 20%.

16.1.1.2 Alternatively, the last four of seven results used in an MDL study may be used as the IDC, if the MDL study was run exclusively by the analyst. ONLY the last four results may be used.

16.1.1.3 If either criterion is not met, locate and correct the source of any problem and repeat the study to confirm the corrective action was successful. Repeated failure however, will confirm a general problem with the procedure or techniques used. If multiple failures occur, correct the procedure or techniques used, and repeat the study.

16.1.1.4 Samples may not be processed by any analyst until an IDC study has been successfully completed. Give copies of successful IDC study spreadsheets and raw data to the quality assurance department for training documentation.

16.1.2 Continuing Demonstration of Capability Study

16.1.2.1 Annually, a Continuing Demonstration of Capability (CDC) study is required by each analyst.

16.1.2.2 A CDC may be accomplished by repeating the IDC study, by using the last four results from an MDL study, or by using four consecutive and exclusively run blank spike results obtained from routine sample analysis since the IDC study was completed. Alternatively, successful completion of an exclusively digested performance testing study result run since completing the IDC may be used.

16.1.2.3 Process CDC data using the same demonstration of capability spreadsheet and in the same manner as the IDC.

16.2 Method Detection Limit Studies

16.2.1 A Method Detection Limit (MDL) study must be performed annually for this procedure. The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence the value is above zero.

16.2.2 The procedure used for an MDL study is based on the method given in the Code of Federal Regulations, Title 40, Part 136, Appendix B, latest revision.

16.2.3 Seven replicate digestions are performed using digestion cups spiked with all elements of interest at the estimated minimum reportable concentration.

16.2.4 The standard deviation of the average for each element, using all seven results is calculated and multiplied by 3.143. The resulting number is the calculated MDL.

16.2.5 If the concentration spiked is between the calculated MDL and ≤10 times the calculated MDL, and there are no zero percent recoveries in the seven results then the MDL passes.

16.2.6 If the MDL study does not pass acceptably, it must be re-digested. If a study needs re-digested at a different concentration, the entire set of seven needs re-digested. If a study does not pass due to poor reproducibility on one result, only that one result needs re-digested. However, only one result of the seven can be re-digested without re-digesting the entire study.

16.2.7 All seven MDL study results do not need digested in the same digestion batch.

17.0 POLLUTION PREVENTION

17.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

17.2 Never dispose of a laboratory chemical without first referencing appropriate written instructions of disposal for that particular material.

17.3 Conserve the use of chemicals where applicable.

17.4 Comply with all environmental laws associated with chemicals in the laboratory.

18.0 WASTE MANAGEMENT

18.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals.

18.2 To minimize the environmental impact and costs associated with chemical disposal, order and use only the minimum amount of material required.

18.3 Follow all instructions in TriMatrix SOP GR-15-102 for laboratory waste disposal requirements.

19.0 REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 2, December 1996, Method 3050B, "Acid Digestion of Sediments, Sludge, and Soils"

20.0 ATTACHMENTS

20.1 ICP Spiking Solution SSW-1A Certificate of Analysis Example

20.2 ICP Spiking Solution SSW-SSS-2A Certificate of Analysis Example

20.3 ICP/MS Spiking Solution A Certificate of Analysis Example

20.4 ICP/MS Spiking Solution B Certificate of Analysis Example

20.5 Work Order Report Example

20.6 Preparation Batch Report Example

Attachment 20.1
ICP Spiking Solution SSW-1A Certificate of Analysis Example

INORGANIC VENTURES

CERTIFICATE OF ANALYSIS

195 Lehigh Avenue, Suite 4
Lakewood, New Jersey 08701 · USA
inorganicventures.com

tel: 800.669.6799 · 732.901.1900
fax: 732.901.1903
info@inorganicventures.com

1.0 **INORGANIC VENTURES** is an ISO Guide 34:2000 registered Certified Reference Material (CRM) Manufacturer (Certificate #883-02). The certificate is designed and the data is determined in accordance with ISO Guide 31:2000 (Reference Materials-Contents of Certificates and Labels), ISO Guide 34:2000 "Quality System Guidelines for the Production of Reference Materials," and ISO Guide 35-1989 "Certification of Reference Materials - General and Statistical Principals."

2.0 **DESCRIPTION OF CRM** Custom Solution

Catalog No.: TRIMATRIX-SSW-1A

Lot Number: **Y-MEB188079**

Matrix: 2% HNO3(abs)

A607108
DA
7-06-06

2,500.00 µg/mL each:
Ca, K, Mg, Na,
250.00 µg/mL each:
Al, As, P, Se, Tl,
50.00 µg/mL each:
Ag, B, Ba, Cd, Co, Cr3, Cu, Fe, Li, Mn, Ni, Pb, Sr, V, Zn,
5.00 µg/mL each:
Be

3.0 **CERTIFIED VALUES AND UNCERTAINTIES**

ELEMENT	CERTIFIED VALUE	ELEMENT	CERTIFIED VALUE	ELEMENT	CERTIFIED VALUE
Aluminum, Al	249.8 ± 0.7 µg/mL	Arsenic, As	250.2 ± 0.8 µg/mL	Barium, Ba	50.16 ± 0.08 µg/mL
Beryllium, Be	5.004 ± 0.010 µg/mL	Boron, B	50.07 ± 0.10 µg/mL	Cadmium, Cd	50.16 ± 0.22 µg/mL
Calcium, Ca	2,500 ± 6 µg/mL	Chromium+3, Cr3	50.11 ± 0.16 µg/mL	Cobalt, Co	50.09 ± 0.12 µg/mL
Copper, Cu	50.17 ± 0.14 µg/mL	Iron, Fe	49.84 ± 0.32 µg/mL	Lead, Pb	50.17 ± 0.11 µg/mL
Lithium, Li	49.91 ± 0.06 µg/mL	Magnesium, Mg	2,501 ± 5 µg/mL	Manganese, Mn	49.97 ± 0.12 µg/mL
Nickel, Ni	50.10 ± 0.12 µg/mL	Phosphorus, P	249.5 ± 0.6 µg/mL	Potassium, K	2,500 ± 5 µg/mL
Selenium, Se	249.8 ± 0.8 µg/mL	Silver, Ag	50.01 ± 0.11 µg/mL	Sodium, Na	2,497 ± 1 µg/mL
Strontium, Sr	50.05 ± 0.11 µg/mL	Thallium, Tl	249.9 ± 0.7 µg/mL	Vanadium, V	49.98 ± 0.14 µg/mL
Zinc, Zn	50.09 ± 0.12 µg/mL				

Certified Density: 1.049 g/mL (measured at 22° C)

The Certified Value is based upon the most precise method used to analyze this CRM. The following equations are used in the calculation of the certified value and the uncertainty:

Certified Value $(\bar{x}) = \frac{\Sigma x_i}{n}$

Uncertainty $(\pm) = \frac{2[(\Sigma s_i)^2]^{1/2}}{(n)^{1/2}}$

$(\bar{x})$ = mean
x_i = individual results
n = number of measurements
Σs_i = The summation of all significant estimated errors (Most common are the errors from instrumental measurement, weighing, dilution to volume, and the fixed error reported on the NIST SRM certificate of analysis.)

Approved By: PD 1-15-09 QA Officer

Approved By: MAS 01-15-09 Area Supervisor

Attachment 20.2
ICP Spiking Solution SSW-SSS-2A Certificate of Analysis Example

INORGANIC VENTURES™ CERTIFICATE OF ANALYSIS

195 Lehigh Avenue, Suite 4
Lakewood, New Jersey 08701 · USA
inorganicventures.com

tel: 800.669.6799 · 732.901.1900
fax: 732.901.1903
info@inorganicventures.com

1.0 **INORGANIC VENTURES** is an ISO Guide 34:2000 registered Certified Reference Material (CRM) Manufacturer (Certificate #883-02). The certificate is designed and the data is determined in accordance with ISO Guide 31:2000 (Reference Materials-Contents of Certificates and Labels), ISO Guide 34:2000 "Quality System Guidelines for the Production of Reference Materials," and ISO Guide 35-1989 "Certification of Reference Materials - General and Statistical Principals."

2.0 **DESCRIPTION OF CRM** Custom Solution

Catalog No.: TRIMATRIX-SSW-SSS-2A

Lot Number: **Y-MEB201134**

Matrix: tr. HF, 2% HNO3(abs)

A609280
DSL 9-11-06
exp. 10-01-07

250.00 µg/mL each:
Sb, Si, Sn,
50.00 µg/mL each:
Mo, Ti

3.0 **CERTIFIED VALUES AND UNCERTAINTIES**

ELEMENT	CERTIFIED VALUE	ELEMENT	CERTIFIED VALUE	ELEMENT	CERTIFIED VALUE
Antimony, Sb	249.1 ± 0.4 µg/mL	Molybdenum, Mo	50.02 ± 0.10 µg/mL	Silicon, Si	249.7 ± 0.8 µg/mL
Tin, Sn	250.6 ± 0.9 µg/mL	Titanium, Ti	50.14 ± 0.08 µg/mL		

Certified Density: 1.015 g/mL (measured at 22° C)

The Certified Value is based upon the most precise method used to analyze this CRM. The following equations are used in the calculation of the certified value and the uncertainty:

Certified Value $(\bar{x}) = \frac{\Sigma x_i}{n}$

Uncertainty $(\pm) = \frac{2[(\Sigma s_i)^2]^{1/2}}{(n)^{1/2}}$

$(\bar{x})$ = mean
x_i = individual results
n = number of measurements
Σs_i = The summation of all significant estimated errors (Most common are the errors from instrumental measurement, weighing, dilution to volume, and the fixed error reported on the NIST SRM certificate of analysis.)

4.0 TRACEBILITY TO NIST AND VALUES OBTAINED BY INDEPENDENT METHODS

· "Property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties." (ISO VIM, 2nd ed., 1993, definition 6.10)

· This product is Traceable to NIST via an unbroken chain of comparisons. The uncertainties for each certified value are reported, taking into account the SRM uncertainty error and the measurement, weighing and volume dilution errors. In rare cases where no NIST SRMs are available, the term 'in-house std.' is specified.

Attachment 20.3
ICP/MS Spiking Solution A Certificate of Analysis Example

ENVIRONMENTAL EXPRESS

Certificate of Analysis

HP2079-1-1L
Solution A
Lot # 605319

Source	Source Purity	Matrix	Standard Concentration
High Purity Metals, Salts or Oxides	99.98+%	HNO_3, 3.5%	mg/L ± 0.5% See element list on reverse

This spectrometric standard solution has been prepared from high-purity reference materials. Sub-boiling distilled high-purity acid has been used to place the materials in solution and to stabilize the standard. The matrix is as noted above in 18 megaohm deionized water. The reference materials have been assayed by inductively coupled plasma optical emission spectrometry (ICP-OES).

The standard has been prepared gravimetrically by weighing the reference material to 5 significant figures. Volumetric glassware has been calibrated gravimetrically to 5 significant figures. The standard concentration has been verified by ICP-OES against an independent source which is traceable to National Institute of Standards and Technology, Standard Reference Material No. 3100 series.

This standard is valid for one year from the shipping date provided the solution is kept tightly capped and stored under normal laboratory conditions.

Theodore C Rains

Theodore C. Rains, Ph.D.
Laboratory Director

A602735
exp 3-31-07
Rec'd 2-28-06

Exp Date: MAR '07
MSDS ATTACHED

490 Wando Park Blvd.
Mt. Pleasant, South Carolina 29464
Phone: 1.843.881.6560
Toll Free: 1.800.343.5319
FAX: 1.843.881.3964
www.environmentalexpress.com

Attachment 20.4
ICP/MS Spiking Solution B Certificate of Analysis Example

ENVIRONMENTAL EXPRESS

Certificate of Analysis

HP2079-1-1L
Solution B
Lot # 605319

Source	Source Purity	Matrix	Standard Concentration
High Purity Metals, Salts or Oxides	99.98+%	HNO_3, 2% + Tr HF	100 mg/L ± 0.5% Antimony, Silicon, Titanium, Molybdenum, Tin

This spectrometric standard solution has been prepared from high-purity reference materials. Sub-boiling distilled high-purity acid has been used to place the materials in solution and to stabilize the standard. The matrix is as noted above in 18 megaohm deionized water. The reference materials have been assayed by inductively coupled plasma optical emission spectrometry (ICP-OES).

The standard has been prepared gravimetrically by weighing the reference material to 5 significant figures. Volumetric glassware has been calibrated gravimetrically to 5 significant figures. The standard concentration has been verified by ICP-OES against an independent source which is traceable to National Institute of Standards and Technology, Standard Reference Material No. 3100 series.

This standard is valid for one year from the shipping date provided the solution is kept tightly capped and stored under normal laboratory conditions.

Theodore C Rains

Theodore C. Rains, Ph.D.
Laboratory Director

A602736
exp 3-31-07
rcvd 2-28-06

MAR '07
Exp Date:
MSDS ATTACHED

490 Wando Park Blvd.
Mt. Pleasant, South Carolina 29464
Phone: 1.843.881.6560
Toll Free: 1.800.343.5319
FAX: 1.843.881.3964
www.environmentalexpress.com

Approved By: RD 1-15-09 QA Officer — Approved By: UAS 01-15-09 Area Supervisor

Attachment 20.5
Work Order Report Example

TriMatrix Laboratories, Inc.

WORK ORDER 0609330

Page 1 of 6

Printed: 7/11/2007 5:32:43PM

Client: [redacted]
Project: [redacted]
Work Order: [redacted]

Project Manager: **Gary L. Wood**
Project Number: **[none]**
SDG:

Report To:
[redacted]

Invoice To:
[redacted]

Client Due Date: **Oct-04-06 16:00 (10 day TAT)**
Date Received: Sep-20-06 12:00 25.9°C
Date Logged In: Sep-21-06 16:37
W.O. Comments: *3FL*
Send cc of report with invoice to Richard Hodge.

Report Level: **3FL**
Received By: William D. Cole
Logged In By: Kristyn N. Courtnay

Analysis	Lab Due Date	TAT	Expires	Analysis Comments
0609330-01 06-35 [Waste] Sampled Sep-12-06 10:00 Eastern				**RCRA 8 Metals (Total & TCLP): Report pHs**
Ag TCLP 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Ag Total 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
As TCLP 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
As Total 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Ba TCLP 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Ba Total 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Cd TCLP 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Cd Total 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Cr TCLP 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Cr Total 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Hg TCLP 7470A	Oct-03-06 17:00	10	Oct-10-06 10:00	
Hg Total 7471A	Oct-03-06 17:00	10	Oct-10-06 10:00	
Pb TCLP 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Pb Total 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Se TCLP 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Se Total 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
TCLP Metals Extraction	Oct-03-06 17:00	10	Sep-26-06 10:00	
0609330-02 06-36 [Waste] Sampled Sep-12-06 10:00 Eastern				**RCRA 8 Metals (Total & TCLP): Report pHs**
Ag SPLP 6010B	Jan-01-80 00:00		Sep-12-06 10:00	Added for SequenceQC in: 6092720
Ag TCLP 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Ag Total 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
As SPLP 6010B	Jan-01-80 00:00		Sep-12-06 10:00	Added for SequenceQC in: 6092720
As TCLP 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
As Total 6010B	Oct-03-06 17:00	10	Mar-11-07 10:00	
Ba SPLP 6010B	Jan-01-80 00:00		Sep-12-06 10:00	Added for SequenceQC in: 6092720

wko_TM_Basic.rpt

Approved By: 1-15-9 **QA Officer**

Approved By: MAS 01-15-09 **Area Supervisor**

Attachment 20.6
Preparation Batch Report Example

TriMatrix Laboratories, Inc.

PREPARATION BATCH 0610939 Page 1 of 3

Printed: 7/11/2007 5:25:28PM

Metals, Waste, 3050B Digestion

(No Surrogate)

Batch Comments: MAS 09/25/06 &:00AM-3:30PM

Work Order	Analysis	Work Order	Analysis	Work Order	Analysis
0609330	Se Total 6010B	0609330	Pb Total 6010B	0609330	Cr Total 6010B
0609330	Cd Total 6010B	0609330	Ba Total 6010B	0609330	As Total 6010B
0609330	Ag Total 6010B				

Lab Number	*Contain*	*Prepared*	*By*	*Initial (g)*	*Final (mL)*	*uL Surrogate*	*Source ID*	*Spike ID*	*uL Spike*	*Client/ QC Type*	*Extraction Comments*
0610939-BLK1		Sep-25-06 07:00	MAS	0.5	50					BLANK	
0610939-BS1		Sep-25-06 07:00	MAS	0.5	50			A607108	250	LCS	
0610939-MS1		Sep-25-06 07:00	MAS	0.5	50		0609330-02	A607108	250	MATRIX SPIKE	
0610939-MS2		Sep-25-06 07:00	MAS	0.5	50		0609330-02	A607109	250	MATRIX SPIKE	
0610939-MSD1		Sep-25-06 07:00	MAS	0.5005	50		0609330-02	A607108	250	MATRIX SPIKE DUP	
0610939-MSD2		Sep-25-06 07:00	MAS	0.5005	50		0609330-02	A607109	250	MATRIX SPIKE DUP	
0609330-01	A	Sep-25-06 07:00	MAS	0.4998	50					[redacted]	
0609330-01	A	Sep-25-06 07:00	MAS	0.4998	50					[redacted]	
0609330-01	A	Sep-25-06 07:00	MAS	0.4998	50					[redacted]	
0609330-01	A	Sep-25-06 07:00	MAS	0.4998	50					[redacted]	
0609330-01	A	Sep-25-06 07:00	MAS	0.4998	50					[redacted]	
0609330-01	A	Sep-25-06 07:00	MAS	0.4998	50					[redacted]	
0609330-01	A	Sep-25-06 07:00	MAS	0.4998	50					[redacted]	
0609330-02	A	Sep-25-06 07:00	MAS	0.5001	50					[redacted]	
0609330-02	A	Sep-25-06 07:00	MAS	0.5001	50					[redacted]	
0609330-02	A	Sep-25-06 07:00	MAS	0.5001	50					[redacted]	
0609330-02	A	Sep-25-06 07:00	MAS	0.5001	50					[redacted]	
0609330-02	A	Sep-25-06 07:00	MAS	0.5001	50					[redacted]	
0609330-02	A	Sep-25-06 07:00	MAS	0.5001	50					[redacted]	
0609330-02	A	Sep-25-06 07:00	MAS	0.5001	50					[redacted]	
0609330-03	A	Sep-25-06 07:00	MAS	0.4995	50					[redacted]	
0609330-03	A	Sep-25-06 07:00	MAS	0.4995	50					[redacted]	

Comments:	Analyst Initials:

bch_TriMatrix.rpt

Approved By: DA 1-15-09 **QA Officer**

Approved By: MAS 01-15-09 **Area Supervisor**

TriMatrix Laboratories, Inc.

UNCONTROLLED COPY

STANDARD OPERATING PROCEDURE

Inductively Coupled Plasma-Mass Spectrometry
Perkin Elmer Elan 6000/6100

SW-846 Method 6020A

APPROVALS:

Area Supervisor: _____ Date: 1-19-09
Denise S. Coffey

QA Officer: _____ Date: 1-15-09
Tom C. Boocher

Operations Manager: _____ Date: 1/19/09
Jeff P. Glaser

Procedure Number: GR-01-129
Revision Number: 3.8

Date Initiated: 12/4/97
Effective Date: 2/1/09

Date Revised: 1/15/09
Pages Revised: All

By: David W. Johnson

Total Number of Pages: 35

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

1.0 SCOPE AND APPLICATION

1.1 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is applicable to a large range of metallic elements in numerous matrices, including but not limited to soil, non-potable water, TCLP extracts, oil, solvents, sludge and air. Most matrices require solubilization or digestion prior to analysis.

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846,* 3rd Edition, Draft Update IVA, May 1998, Method 6020A, "Inductively Coupled Plasma – Mass Spectrometry", Revision 1, January 1998

3.0 SUMMARY OF PROCEDURE

3.1 Prior to analysis, samples are solubilized or digested using appropriate sample preparation. Refer to TriMatrix standard operating procedures for metals sample preparation and digestion.

3.2 This procedure describes the multi-elemental determination of analytes by ICP-MS. The procedure measures ions produced by a radio frequency inductively coupled plasma. Sample material in solution is introduced by pneumatic nebulization into radio-frequency plasma where energy transfer processes cause desolvation, atomization and ionization. Ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of mass-to-charge ratio by a quadrupole. Ion detection is by an electron multiplier or Faraday detector and the information is processed through data handling software.

3.3 Interferences must be assessed and valid corrections applied, or the data flagged to indicate problems. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or from the sample matrix. Instrumental drift, suppressions or enhancements of instrument response caused by the sample matrix must be corrected by the use of internal standards.

4.0 PARAMETER OR COMPOUND LIST

4.1 This procedure may be used for analysis of the following metals.

Aluminum	Barium	Cadmium	Copper	Molybdenum	Silver	Vanadium	Strontium
Antimony	Beryllium	Chromium	Lead	Nickel	Thallium	Zinc	Gold
Arsenic	Boron	Cobalt	Manganese	Selenium	Tin	Uranium	Zirconium

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal*, latest revision

5.2 ELAN 6000 *Software Guide*; Perkin Elmer Corporation, Manual 0993-8965, Release E, June 1995

5.3 ELAN 6000 *Hardware Guide*; Perkin Elmer Corporation, Manual 0993-8969, Release D, September 1995

5.4 TriMatrix SOP GR-01-137, *Acid Digestion of Sediments, Sludges, Soils and Organic Waste using Block Digestion*, latest revision

5.5 TriMatrix SOP GR-01-144, *Block Digestion of Antimony in Sediments, Sludges and Soils*, latest revision

5.6 TriMatrix SOP GR-01-147, *Acid Digestion of Total/Dissolved Water TCLP/SPLP Extract and Wastewater by Block Digestion for ICP Total Metals Analysis Acid Digestion of Total/Dissolved Water and TCLP/SPLP Extract By Block Digestion for ICP/MS Total Metals Analysis*, latest revision

5.8 TriMatrix SOP GR-10-106, *Inorganic and Metals Laboratories Corrective Actions*, latest revision

5.9 TriMatrix SOP GR-10-123, *Element™ Data Transfer and Review*, latest revision

5.10 TriMatrix SOP GR-10-125, *Method Detection Limit (MDL)*, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). All elements determined by this procedure have at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use, only molybdenum^{98} (ruthenium) and selenium^{82} (krypton) have isobaric elemental interferences. If alternative isotopes having higher natural abundance are selected to achieve greater sensitivity, an isobaric interference may occur. A data software system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element, and subtracting the appropriate signal from the analyte isotope signal. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for calculations. Relevant isotope ratios must be established prior to the application of any corrections. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, analysis using another verified and documented isotope, or use of another method.

6.2 Abundance sensitivity is a property defining the degree to which mass peak wings contribute to adjacent masses. Abundance sensitivity is affected by ion energy and quadropole operating pressure. Wing overlap interferences may result when a small ion peak is measured adjacent to a large one. The potential for these interferences must be recognized and spectrometer resolution adjusted to minimize them.

6.3 Isobaric molecular and doubly charged ion interferences in ICP-MS are caused by more than one atom or charge, respectively. Most isobaric interferences that affect ICP-MS determinations have been identified in the literature. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using natural

isotope abundances from the literature, the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<2%) counting statistics. Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride corrections for arsenic can be calculated (approximately) as follows, where the $^{38}Ar^{37}Cl+$ contribution at m/z is negligible 0.06% of the $^{40}Ar^{35}Cl+$ signal:

Corrected arsenic signal (using natural isotope abundances for coefficient approximations) =
[(m/z 75 signal)-((3.13)(m/z 77 signal))+((2.73)(m/z 82 signal))

Where the final term "((2.73)(m/z 82 signal))" adjusts for any selenium contribution at m/z 77

6.3.1 Cadmium values will be biased low by this type of equation when $^{97}ZrO^+$ ions contribute at m/z 108, but m/z 111 for cadmium is even subject to direct ($^{94}ZrO^+$) additive interferences when Zr is present.

6.3.2 The coefficients in the cadmium equation are ONLY illustrative for the arsenic equation above. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for the standard solution at a concentration providing suitable (<1%) counting precision.

6.3.3 The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found to be reliable. For example, oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by use of an appropriate oxide as the interferent. This type of correction has been reported for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas has been shown to greatly reduce molecular interferences. These techniques can be used provided reporting limits, accuracy and precision requirements for analysis can be met.

6.3.4 If analysis requirements are not met, ionic interference is corrected based on actual instrument response instead of literature equations. Instrument-derived equations may be updated as needed without change to the standard operating procedure.

6.3.5 Ionic interference corrections are printed with each quantitative analysis calibration report after the correlation coefficient report. Refer to Attachment 23.11 for an ionic interference correction report example.

6.4 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended to minimize solid deposition. An internal standard can be used to correct for physical interferences if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes.

6.5 Memory interferences – Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones and from material buildup in the plasma torch and spray chamber. The site where these effects occur is element dependent and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interference must be recognized within an analytical run and suitable rinse times used to reduce them. Memory interferences must be monitored within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alert to the possibility of a memory effect and must examine analyte concentration in the previous sample to identify if this was high. If memory interference is suspected, the sample must be reanalyzed after a long rinse period.

7.0 SAFETY PRECAUTIONS

7.1 Analysts must comply with all standard operating procedures for health and safety as outlined in the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan.

7.2 Concentrated acids are used in the preparation of standards and samples for analysis by ICP-MS. Disposable gloves, laboratory coats and approved safety glasses must be worn at all times when handling concentrated acids. Disposable gloves must also be worn when handling digested samples. Refer to the MSDS for information on these or any other chemical utilized in this procedure.

7.3 Check the exhaust hood over the instrument to be sure it is operating correctly. If the ventilation system is not working properly, extinguish the plasma if lit and immediately contact the metals laboratory manager. Under no circumstances must the ICP-MS be used if the exhaust hood is not working.

7.4 The plasma emits UV radiation. Avoid looking directly at the plasma without some type of strong UV protection. The instrument uses a UV resistant material in the viewing port so the analyst may watch the plasma. Do not tamper with this plate. Do not operate the machine without this plate in place. Do not attempt to view the plasma directly or indirectly in any way. Failure to follow this policy may cause serious and immediate damage to the retina of the eye and will result in disciplinary action.

7.5 The ICP-MS emits a strong RF field. To minimize exposure to this field, Perkin Elmer has included several safety interlocks to prevent direct exposure to harmful radiation. Never override any interlock on the ICP-MS. When working on the instrument, replace all RF shielding using all supplied screws. If any safety device has been tampered with, contact the metals lab manager.

7.6 The ICP uses argon to sustain plasma and to nebulize sample. Argon can cause suffocation through oxygen replacement. It is therefore imperative that all sources of argon be turned off with a valve when not in use. Since argon is colorless and odorless, if a feeling of lightheadedness develops, evacuate the metals laboratory at once and notify the area supervisor and/or the health and safety officer. Refer to the MSDS for information on this or any chemicals utilized.

7.7 All elements used in this procedure are toxic. Refer to the MSDS for information on these or any other chemicals utilized in this procedure.

7.8 No food or drink is allowed in the metals laboratory.

7.9 Wash hands before starting work. Chemicals may be present on the skin, which may interfere with metals analysis. Wash hands before leaving the metals laboratory. Chemicals and acids may be on the skin that could eventually be ingested or passed on to a second party through casual contact.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Aqueous samples should have been acidified at the time of collection to a pH of <2. If the pH is not <2 when received by the laboratory, the sample pH must be lowered to <2 during the sample receipt process. A minimum of 24 hours must elapse after adjustment prior to sample digestion.

8.2 Solid samples require no preservation for metals. However, if the same sample container is scheduled for other analyses where refrigeration of the sample is needed, store at 4 ±2° C.

8.3 Samples may be collected in glass or polyethylene. If Silicon or Boron is to be analyzed, polyethylene containers must be used. Acidified sample must never come into contact with metal, to prevent contaminants leaching into the sample.

8.4 For dissolved metals analysis, the sample should have been filtered on site and acidified to pH <2. If pH is not <2, the sample pH must be lowered to <2 at sample receipt and a minimum of 24 hours must elapse after the adjustment, before analyzing the sample.

8.5 Holding times for all metals for ICP-MS is 180 days. In the case of TCLP or similar extracts, the holding time starts at the time leachate is generated.

8.6 The minimum sample volume for this procedure is 50 mL and 150 mL if samples require matrix QC. Samples must be solubilized prior to analysis. A smaller minimum volume is required if a sample will need diluted due to high concentration. Small minimum volumes sacrifice the reporting limit.

8.7 Digested (solubilized) samples and undigested acidified aqueous samples need not be refrigerated. All samples must be at room temperature prior to digestion. All digestates must be at room temperature prior to analysis.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Perkin Elmer, ELAN 6000/6100 inductively coupled plasma mass spectrometers (ICP-MS):

9.1.1 Both instruments are capable of scanning the mass range 6-240 amu with a minimum resolution of 1 amu peak width at 10% peak height. Both instruments are fitted with an extended dynamic range detection system. The instruments also include an ELAN data system capable of making corrections for isobaric interferences and application of the internal standards technique.

NOTE: Electron multiplier detectors are used and precautions must be taken to prevent exposure to high ion flux. Otherwise changes in instrument response or damage to the multiplier may result.

9.1.2 Radio-frequency generators are used, compliant with FCC regulations.

9.1.3 A variable-speed peristaltic pump delivers solution to the nebulizer.

9.1.4 A mass-flow controller on the nebulizer gas supply is used.

9.2 Analytical balance with the capability of measuring to 0.1 mg for use in weighing solids, for preparing standards and for determining dissolved solids in digestates or extracts.

9.3 A Recirculator/chiller (Neslab CFT750). Temperature must be maintained at 18° C and pressure must be 35-60 psi. The recirculator is attached directly to the mass spectrometer to maintain isothermal conditions.

9.4 Centrifuge tubes (15 mL, clear) or equivalent. The tube must stand upright within the autosampler rack without tipping or leaning.

9.5 Eppendorf micropipettes capable of delivering 5-1000 uL

9.6 Flasks, Class A volumetric, various sizes

9.7 Pipettes, Class A, glass, various sizes

9.8 Balance, top-loading, capable of measurement to two decimal places.

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 All maintenance activities must be recorded in the instrument maintenance logbook. Refer to Attachment 23.1 for an example instrument maintenance logbook.

10.2 At the beginning of each shift (every 8 hours) the manifold pump tubing must be replaced.

10.3 There are two filters on the ELAN 6000/6100 that must be replaced periodically. The two filters are located on the back of the instrument.

10.4 Inspect the waste container on the floor by the instrument every shift. If the jug is full, properly dispose of the liquid.

10.5 Visually inspect the torch before lighting the instrument. Do not touch or move the torch. <u>The inspection must be visual only.</u>

10.5.1 Open the vacuum chamber.

10.5.2 Observe the torch. If the torch is broken or cracked, replace it. Refer to Section 10.6 for discussion on how to assemble and disassemble the torch.

10.5.3 Listen for obvious leaks in the argon lines going to the torch and nebulizer. If leaks are heard, investigate them and tighten the fittings to stop the leak. If a leak cannot be found or cannot be stopped, contact the metals laboratory manager.

10.6 Once every four to eight weeks disassemble the entire torch assembly and inspect all parts for wear. Replace all worn or damaged parts. Record all changes in the instrument maintenance logbook.

10.6.1 Turn off the plasma if it is on by selecting instrument, front panel, and then stop on the plasma box. The pump will stop when the plasma is extinguished.

10.6.2 Turn off the RF Generator by turning off the circuit breaker labeled RF Generator (CB1) on the left side of the instrument.

10.6.3 Loosen the retaining ring and remove the spray chamber assembly.

10.6.4 Open the top left cover of the ELAN. Use a flat blade screwdriver on the release mechanism to release the vacuum chamber interlock lever. Grasp the lever and pull in counter clockwise direction to slide the vacuum chamber and interface away from the torch box.

10.6.5 Remove the gas line connections from the torch by loosening the Swagelock fittings. Slide the fittings and connection tubing up and off the torch.

10.6.6 To remove the torch assembly, rotate the torch mount 1/8 turn counter clockwise and remove the entire assembly through the right side of the torch box.

10.6.7 With one hand grasping the torch and the other holding onto the Lexan adapter, twist and pull back on the adapter to separate the adapter from the torch.

10.6.8 Inspect all O-rings and replace any that are cracked or damaged.

10.6.9 Remove the alumina injector. If it is dirty, wash with soap and water. Dry, then put in the muffle furnace at 700° C for 20 minutes.

10.6.10 If the torch is dirty, immerse in an ultrasonic cleaner containing 1% nitric acid. Rinse with metals laboratory reagent water. Replace any torch that cannot be cleaned or is damaged.

10.6.11 After having been cleaned or replaced, reposition and align the ICP torch as follows:

10.6.11.1 Slide the injector/support adapter to the back of the torch.

10.6.11.2 Place the torch through the hole in the right side of the torch box. Rotate the torch assembly 1/8 turn clockwise until the bayonet mount is fully seated.

10.6.11.3 Reattach the gas lines to the ICP torch. Slide both fittings and connecting tubing onto the torch and tighten the Swagelock fittings several turns.

10.6.11.4 To check the torch position and measure for proper alignment, follow Sections 10.6.11.5 through 10.6.11.8.

10.6.11.5 Place the torch alignment tool on the torch so the alignment tool flange touches the first turn of the load coil. Loosen the torch locking collar approximately 1 cm and slide the torch until it lines up with the outer edge of the alignment tool.

10.6.11.6 Slide the tool out approximately 1/2 inch and using the lever, move the vacuum chamber interlock into the lock position.

10.6.11.7 Move the vacuum chamber to the closed position to locate the alignment tool within the load coil.

10.6.11.8 Move the chamber to the open position and adjust the vacuum chamber position so the top end of the torch is even with the 5.5 mm cutout depth of the alignment tool.

10.6.11.9 If the torch is not properly lined up, loosen the two locking screws of the vacuum chamber interlock. Adjust the vacuum chamber forward or backward until the proper position is achieved.

10.6.11.10 Slide the vacuum chamber and interface toward the torch box. Secure the vacuum chamber interlock and close the top cover.

10.6.11.11 Turn on the RF Generator by turning on the circuit breaker labeled RF Generator (CB1) on the side of the instrument.

10.6.12 Inspect the drain line at the base of the spray chamber. There must be no leaks or cracks in the tubing. If a problem exists, replace the O-ring in the drain cap.

10.6.13 Inspect the nebulizer for wear.

10.6.13.1 If present, remove salt deposits with water.

10.6.13.2 If a cross-flow nebulizer is used, check the tips for wear. Replace the tips if excessive wear is noted.

10.7 Inspect the print quality of the printer. If the print is hard to read or light in appearance, replace the printer cartridge with the appropriate cartridge.

11.0 CHEMICALS AND REAGENTS

11.1 Acids used in standards preparation and for sample processing must be trace metal grade or better. Redistilled acids may be used if demonstrated to be free of contamination.

11.1.1 Concentrated Nitric acid, trace metal grade (Fisher catalog A509-212 or equivalent)

11.1.2 Concentrated Hydrochloric acid, trace metal grade(Fisher catalog A508 or equivalent)

11.2 ASTM Type II water (ASTM D1193): Deionized water is fed into a Barnstead glass distillation unit (Model FI-Streem2). The resulting distillate is immediately transferred to a high density polyethylene carboy. Impurities are measured by the metals group at TriMatrix. This is the only water acceptable for use in the Metals laboratory for dilutions and standard preparation.

11.3 Argon gas supply: Welding grade or better. This is plumbed from a liquid argon tank located outside of the building. Argon is used as the main plasma gas, the auxiliary plasma gas, the nebulizer carrier gas and the RF coil coolant.

12.0 STANDARDS PREPARATION

12.1 All standards must be matrix matched as closely as possible to samples and/or sample digestates. All stock standards expire one year after receipt or on the vendor's expiration date, whichever is earlier.

12.2 Two calibration stock solutions identified as QCA and QCB are purchased at certified concentrations of 100 mg/L containing the following elements.

HP2079-1-1L Solution A (QCA)	Aluminum	Beryllium	Chromium	Lead	Selenium	Thallium
	Arsenic	Boron	Cobalt	Manganese	Silver	Vanadium
	Barium	Cadmium	Copper	Nickel	Strontium	Zinc

HP2079-1-1L Solution B (QCB)	Antimony
	Molybdenum
	Tin

12.3 Second-source stock solutions used as the secondary calibration verification (SCV) are purchased as single-element certified solutions at concentrations of 1000 or 10,000 mg/L from an alternate source/vendor.

12.4 The exception to the above is that uranium, gold and zirconium stock calibration and second-source standards are both purchased as single-element certified solutions.

12.5 All working standards and working standard dilutions for the ICP-MS prepared from stock standard solutions expire 24 hours from the time of preparation.

12.6 Prepare all standards using metals-free ASTM Type II water acidified to 1% with trace-metals grade nitric acid (HNO_3). The acidified water is prepared by adding 10 mL concentrated HNO_3 to 1000 mL ASTM Type II water.

12.7 Prepare uranium, gold and/or zirconium 100 ug/L standards as follows:

12.7.1 Label one bottle "100 mg/L U, Au and/or Zr stock std" then tare on the analytical balance.

12.7.2 Transfer 50 g of 1% acidified ASTM type II water to the bottle.

12.7.3 Pipette 1.0 mL of 10000 mg/L U, Au and/or Zr stock standard into the bottle then add acidified water until the final mass is 100 g.

12.8 Prepare intermediate and working standards of QCA and/or QCB with U, Au and/or Zr using the acidified water. Rinse nine 125 mL polyethylene bottles with acidified water.

12.8.1 Label one bottle 100 ug/L. Tare the bottle on an analytical balance. Pour 50 g of 1% acidified ASTM Type II water into the bottle. Pipette 100 µL of each 100 mg/L standard (labeled QCA, QCB and U, Au and/or Zr) into the bottle. Add acidified water until the final mass is 100 g.

12.8.2 Label one bottle 50 ug/L. Tare the bottle on an analytical balance. Pour 50 g of acidified ASTM Type II water into the bottle. Pipette 50 µL of each 100 mg/L standard (labeled QCA, QCB and U, Au and/or Zr) into the bottle. Add acidified water until the final mass is 100 g.

12.8.3 Label one bottle 20 ug/L. Tare the bottle on an analytical balance. Pour 50 g of acidified ASTM Type II water into the bottle. Pipette 20 µL of each 100 mg/L standard (labeled QCA, QCB and U, Au and/or Zr) into the bottle. Add acidified water until the final mass is 100 g.

12.8.4 Label one bottle 10 ug/L. Tare the bottle on an analytical balance. Pour 50 g of acidified ASTM Type II water into the bottle. Pipette 10 µL of each 100 mg/L standard (labeled QCA, QCB and U, Au and/or Zr) into the bottle. Add acidified water until the final mass is 100 g.

12.8.5 Label one bottle 1.0 ug/L. Tare the bottle on an analytical balance. Pour 50 g of acidified ASTM Type II water into the bottle. Pipette 1000 µL of the 100 ug/L standard into the bottle. Add acidified water until the final mass is 100 g.

12.8.6 Label one bottle 0.2 ug/L. Tare the bottle on an analytical balance. Pour 50 g of acidified ASTM Type II water into the bottle. Pipette 200 µL of the 100 ug/L standard into the bottle. Add acidified water until the final mass is 100 g.

12.8.7 Label one bottle 0.04 ug/L. Tare the bottle on an analytical balance. Pour 50 g of acidified ASTM Type II water into the bottle. Pipette 40 µL of the 100 ug/L standard into the bottle. Add acidified water until the final mass is 100 g.

12.8.8 Label one bottle a blank. Tare the bottle on the analytical balance. Pour 100 g of acidified ASTM Type II water into the bottle.

12.8.9 Record all standard preparations in the standards logbook (Refer to Attachment 23.2).

12.9 Prepare Interference Check Standard A (IFA) as follows:

12.9.1 The IFAs are prepared to contain known concentrations of interfering elements that demonstrate the magnitude of interferences and provide an adequate test of any correction of false positives. Chloride in the IFA provides a means to evaluate software corrections for chloride-related

interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Iron is used to demonstrate adequate resolution of the spectrometer for manganese determinations. Molybdenum serves to indicate oxide effects on cadmium isotopes. Other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The IFA is used to verify that interference levels are corrected by the data system, within quality control limits.

12.9.2 Stock IFA solution is currently purchased from Inorganic Ventures with the following concentrations:

12.9.2.1 6020ICS-OA contains 10,000 mg/L Cl^-, 2000 mg/L C, 1000 mg/L Al, Ca, Fe, Mg, P, K, Na, S, 20 mg/L Mo and Ti as interferents.

12.9.3 Working IFA and IFB solutions must be prepared fresh daily.

12.9.3.1 IFA is prepared by pipetting 100 µL of 6020ICS-OA to 9.9 mL of 1% acidified water.

12.9.3.2 IFB is prepared by pipetting 100 µL of 6020ICS-OA and 20 µL of each SCV stock prepared in section 12.10 to 9.9 mL of 1% acidified water.

12.10 Prepare an SCV Stock Standard Solution as follows:

12.10.1 Rinse three 125 mL polyethylene bottle with 1% nitric acid and tare on the analytical balance.

12.10.2 Transfer approximately 50 g of 1% nitric acid into the bottles.

12.10.3 Pipette 100 µL of each of the following 10000 mg/L second source stock standards into first bottle:

Aluminum	Barium	Cadmium	Copper	Nickel	Thallium	Zinc
Arsenic	Beryllium	Chromium	Lead	Selenium	Silver	Uranium
Strontium	Boron	Cobalt	Manganese	Vanadium	Gold	Zirconium

12.10.4 Pipette 100 µL of 10000 mg/L second source stock standards Antimony and Molybdenum into second bottle.

12.10.5 Pipette 100 µL of 10000 mg/L second source stock standard Tin into the third bottle.

12.10.6 Dilute all three bottles to 100 g with 1% nitric acid.

12.10.7 Concentration for each element is 10 mg/L.

12.11 Prepare the SCV working solution as follows:

12.11.1 Rinse a 125 mL polyethylene bottle with 1% acidified water.

12.11.2 Tare the bottle on an analytical balance.

12.11.3 Transfer 50 g of 1% acidified ASTM Type II water into the bottle.

12.11.4 Pipette 400 µL of each SCV Stock Standard solution into the bottle then add 1% acidified water until the final mass is 100 g.

12.11.5 Refer to Attachment 23.6 for concentrations.

12.12 Prepare Internal Standard Solution as follows:

12.12.1 For the ELAN 6000, pipette 1600 µL Lithium, 400 µL Germanium, 40 µL Indium, 40 µL Terbium, 60 µL Bismuth, 60 µL Rhodium and 40 µL Holmium into 1000 mL of 1% acidified ASTM Type II water.

12.12.2 For the ELAN 6100, pipette 1000 µL Lithium, 300 µL Germanium, 30 µL Indium, 20 µL Terbium, 40 µL Bismuth, 30 µL Rhodium and 20 µL Holmium into 1000 mL of 1% acidified ASTM Type II water.

12.12.3 Internal standard concentrations may be changed at any time, if changing the concentration generates a more appropriate intensity.

12.13 Prepare tuning intermediate solution as follows:

12.13.1 Rinse a 100 mL polyethylene bottle with 1% nitric acid and tare on the analytical balance.

12.13.2 Transfer approximately 50 g 1% nitric acid.

12.13.3 Pipette the following standards into the bottle:

12.13.3.1 100 µL of 10000 mg/L beryllium

12.13.3.2 100 µL of 10000 mg/L magnesium

12.13.3.3 100 µL of 10000 mg/L cobalt

12.13.3.4 100 µL of 10000 mg/L lead

12.13.3.5 100 µL of 10000 mg/L barium

12.13.3.6 10 µL of 1000 mg/L cerium

12.13.4 Add 1% nitric acid) to a final mass of 100 g. Cap the bottle and shake.

12.13.5 Rinse a 1000 mL polyethylene bottle with 1% nitric acid and tare on the top-loading balance.

12.13.6 Transfer approximately 500 g 1% nitric acid.

12.13.7 Pipette the following standards into the bottle:

12.13.7.1 10 µL of 1000 mg/L indium

12.13.7.2 1000 µL of 6020A intermediate solution

12.13.8 Add 1% nitric acid) to a final mass of 1000 g. Cap the bottle and shake.

13.0 SAMPLE PREPARATION

13.1 Soil, sludge and waste samples must be digested according to method 3050B prior to analysis. Refer to TriMatrix SOP GR-01-137 and GR-01-144.

13.2 Aqueous samples that need digested such as groundwater, TCLP and SPLP must be digested according to method 3010A. Refer to TriMatrix SOP GR-01-147.

13.3 Air samples are digested as specified by the method used in sample collection.

13.4 Any dissolved metals sample having an odor, precipitate or turbidity greater than 1 NTU after filtering must be digested prior to analysis.

14.0 CALIBRATION PROCEDURES

14.1 The ELAN 6000 and 6100 must be calibrated for every analytical run or every 24 hours, whichever is more frequent.

14.1.1 Initial calibration consists of an 8-point calibration curve for silver and cadmium. A 7-point curve is used for all other elements. An initial calibration curve consists of the standard series prepared in Section 12.4. Silver and cadmium curves include the 0.04 ug/L standard. This concentration is not included in the calibration for other elements. The 0 ug/L blank is included as a standard in all calibrations.

14.1.2 The average of at least three plasma responses for each concentration is used in generating calibration curves.

14.1.3 In all cases, calibration is performed using a multi-point linear regression. The correlation coefficient (r) must be greater than or equal to 0.995. If the coefficient is less than 0.995, recalibrate or postpone analysis (for only the out-of-control elements) until an acceptable calibration can be attained.

14.1.4 The highest concentration in the calibration range must not exceed 90% of the linear range (refer to Section 18.10).

14.2 After calibration, an Initial Calibration Verification is performed.

14.2.1 Analyze the Second-Source Calibration Verification (SCV). The SCV must be prepared from an independent (second source) material to a concentration near the mid-point of the calibration curve. The SCV control window is 90%-110% of the expected value. If percent recovery of any target element does not fall within the control window, recalibrate the instrument and restart analysis at Section 14.2 or postpone analysis (for only the out-of-control elements) until an acceptable calibration can be obtained.

14.2.2 Analyze the Initial Calibration Blank (CCB). A CCB is quantitation of the 0 ug/L blank (prepared in Section 12.4.9), as a sample. The absolute value of the CCB reading must be less than 1/5th the minimum reporting limit required for analysis. If the CCB is not lower than 1/5th the reporting limit, recalibrate the instrument and start again at Section 14.2 or postpone analysis (for only out-of-control elements) until an acceptable calibration can be generated. If the ICB remains out-of-control, see the metals laboratory supervisor.

14.2.3 Analyze the MRL-level Calibration Verification (CRL). A CRL is a reporting level standard with a concentration at the minimum reporting limit (MRL). The control window is 50%-150% of the expected value. If percent recovery falls outside the 50-150% window, a narrative must be attached to the analytical batch.

14.2.4 Analyze the IFA solution which is comprised of interfering elements only. The IFA demonstrates the magnitude of interferences and provides a test of any corrections made. Control limits for the IFA are ±3 times the reporting limit for non-spiked elements.

14.2.5 Analyze Interference Check Standard B (IFB). The IFB contains a known concentration of interfering elements that monitors analyte recovery and/or detection, and provides a test for any corrections that need done.

14.2.5.1 Control limits are 90-110% of the known concentration and ±3 times the reporting limit for non-spiked elements.

14.2.5.2 If the IFB is outside a control limit, stop the analysis and remake the solution then re-analyze successfully to continue with sample analysis.

14.2.5.3 If the IFB fails again, generate an acceptable calibration and repeat the analysis for all out-of-control elements. Alternatively, postpone analysis until an acceptable calibration can be generated.

14.2.6 Following the IFB, analyze a Continuing Calibration Verification (CCV) standard. A CCV is the same solution as the SCV. The control window is 90%-110% of the expected value. If the CCV is not within the control window, stop the analysis and re-analyze one time. If the CCV re-analysis is within the control window, continue the analysis. If the CCV remains out-of-control, recalibrate the instrument for the affected elements and restart the analysis at Section 14.2 or postpone analysis (for only out-of-control elements) until an acceptable calibration can be generated.

14.2.7 Follow the CCV with analysis of a Continuing Calibration Blank (CCB). A CCB is quantitation of the 0 ug/L blank prepared in Section 12.4.9, as a sample. The absolute value of the CCB reading must be less than 1/5th the lowest reporting limit required for analysis. If the CCB is not lower than 1/5th the reporting limit, stop the analysis and re-analyze one time. If the CCB re-analysis is less than 1/5th the reporting limit, continue sample analysis. If the CCB remains out-of-control, recalibrate the instrument for the affected elements and restart the analysis at Section 14.2 or postpone analysis (for only out-of-control elements) until an acceptable calibration can be generated.

14.2.8 Analyze up to ten samples. If percent RSD for any result obtained from the replicate plasma response is >20, the sample run immediately prior to the result must be checked for high analyte concentration. If the analyte is high, check the triple-replicate result in question to verify that concentration is not decreasing. If concentration is decreasing, reanalyze the sample. If the concentration is not decreasing, report the result in question.

14.2.9 After each analysis of up to ten samples, analyze the CCV. If the CCV is not within the control window, stop the analysis and re-analyze one time. If CCV re-analysis is within the control window, continue sample analysis. If CCV re-analysis is out-of-control, recalibrate the instrument and start again at Section 14.2 or postpone analysis (for only out-of-control elements), until an acceptable calibration can be generated. All samples associated with an unacceptable CCV must be re-analyzed for all affected target elements.

14.2.10 After each CCV, analyze the CCB. If a CCB is not less than 1/5th the reporting limit, stop the analysis and re-analyze one time. If CCB re-analysis is within the control window, continue sample analysis. If CCB re-analysis is out-of-control, recalibrate the instrument and start again at Section 14.2 or postpone analysis (for only out-of-control elements), until an acceptable calibration can be generated. All samples associated with an unacceptable CCB must be re-analyzed for all affected target elements.

14.2.11 Repeat Sections 14.2.8 through 14.2.10 until all samples have been run. The analytical run must be concluded with analysis of acceptable CCV and CCB results.

14.2.12 The IFA and IFB solutions must be re-verified if an analytical run exceeds 12 hours.

15.0 ANALYTICAL PROCEDURE

15.1 The following sections assume the user to be familiar with ELAN 6000/6100 operating software. If unfamiliar or unsure of any particular part of the operation, consult the instrument manual for additional instructions. This section provides adequate instruction for normal instrumental operation but is not intended to replace the instrument operating manual.

15.2 Preliminary treatment of all sample matrices is almost always necessary to solubilize analyte.

15.2.1 Digestions are referenced in Section 5.0.

15.2.2 A minimum of five internal standards must always used.

15.3 Once the plasma has been on for at least 30 minutes, daily tuning of the instrument needs performed. However, if the sample and skimmer cones have been changed, a more rigorous tune needs performed as follows:

15.3.1 Realign the x and y cone axis.

15.3.2 Optimize the nebulizer flow and lens voltage.

15.3.3 Tune the mass spec over the entire mass range.

15.3.4 Check instrument performance:

15.3.4.1 The instrument will take six readings to generate a percent relative standard deviation (RSD) value for lithium, cobalt, indium and thallium. For each element, RSD must be less than 5.0. If not, repeat the evaluation once. If any element is greater than or equal to 5.0, locate and correct the problem before proceeding.

15.3.4.2 Calculate Percent Ba^{2+}/Ba^{0} and CeO/Ce^{0}. If either criterion is greater than or equal to 3.0%, repeat the check once. If one or the other remains out of limits, locate and correct the problem then repeat the tune.

15.4 Once all tune optimization steps are complete, calibrate in accordance with Section 14.0 and run samples.

16.0 CALCULATIONS AND DATA HANDLING

16.1 The concentration of each sample is read directly from the computer printout. Dilution factors must be taken into account in the ID weight file.

16.1.1 If the digestion or subsequent dilution factors were not included in the sample information file, use the following calculation:

$$C_{Final} = C_{Instr} \times DF_{Digest} \times DF_{Subseq}$$

where:
C_{Final} = Final reported element concentration in ug/L or mg/kg
C_{Instr} = Concentration read from the instrument data printout in ug/L
DF_{Digest} = Digestion dilution factor in mL/mL or mL/g
DF_{Subseq} = Dilution done subsequent to the digestion in mL/mL

16.2 All samples must be reported to the correct number of significant figures. Significant figure truncation must not be performed until all data calculations have occurred.

16.2.1 Solid samples must be reported in mg/kg.

16.2.1.1 For sample concentrations <100 mg/kg, report 2 significant figures.

16.2.1.2 For sample concentrations ≥100 mg/kg, report 3 significant figures.

16.2.1.3 For QC always report one additional significant figure.

16.2.2 Aqueous samples must be reported in ug/L.

16.2.2.1 For sample concentrations <1.0 ug/L, report 1 significant figure.

16.2.2.2 For sample concentrations ≥1.0 ug/L and <100 ppb, report 2 significant figures.

16.2.2.3 For sample concentrations ≥100 ug/L, report 3 significant figures.

16.2.2.4 For QC always report one additional significant figure.

16.2.3 Leachates must be reported in mg/L.

16.2.3.1 For sample concentrations <0.001 mg/L, report 1 significant figure.

16.2.3.2 For sample concentrations ≥0.001 mg/L and <0.10 mg/L, report 2 significant figures.

16.2.3.3 For sample concentrations ≥0.10 mg/L, report 3 significant figures.

16.2.3.4 For QC always report one additional significant figure.

16.3 Whenever possible, calculate a result from both primary and secondary isotopes. Report only the primary isotope result. However, if there is greater than 25% relative difference between the two values, report the lowest value as the result. Monitor relative percent difference as follows:

$$\frac{\text{primary ion} - \text{secondary ion}}{\text{primary ion} + \text{secondary ion}} \Bigg| 200 = \text{relative percent difference (RPD)}$$

17.0 DATA REPORTING AND DELIVERABLES

17.1 Analysts running samples are responsible for correctly filling in, handing in and filing all associated paperwork. It is essential to perform these tasks conscientiously to provide clients with defensible data.

17.2 Report data to the laboratory information management system (Element™) in accordance with TriMatrix SOP GR-10-123.

17.2.1 Data must be recorded completely to ensure that results are reported correctly and data is associated with the right quality control batch. It is important that all required information be recorded correctly and completely.

17.2.2 Quality control information must be completed and recorded including spiked concentrations where applicable.

17.2.3 If internal chain-of-custody (CoC) is required, it is important that CoC forms be filled in correctly and archived appropriately. Refer to Attachment 23.5 for an internal CoC form example.

17.2.4 All analysis hardcopy and benchsheets must be archived appropriately.

17.3 Laboratory Required Paperwork

17.3.1 All run and maintenance logbooks must be filled in completely and correctly. Corrections must be made with a lineout, not a write-over, and must be dated and initialed. Blank lines in logbooks must be Z'd out.

18.0 QUALITY ASSURANCE

18.1 All quality control data must be maintained and available for easy reference or inspection.

18.2 Instrument detection limit (IDL) studies must be performed quarterly.

18.2.1 Analyze seven sequential aliquots of metals reagent water. Repeat on two more non-consecutive days to obtain 21 results in 3 datasets.

18.2.2 Input these data to the IDL spreadsheet located on the laboratory intranet to calculate the IDL which is the calculated average standard deviation.

18.2.3 The spreadsheet compares the calculated IDL to the calculated MDL. The IDL must be less than the MDL. If not, locate the source of the problem and repeat the IDL/MDL studies successfully. Repeat only for elements that failed.

18.2.4 Consult the metals supervisor and/or the quality assurance department if repeated studies indicate the IDL is not less than the MDL.

18.3 Dilute and re-analyze samples that are more concentrated than the highest standard on the calibration curve.

18.4 Include a minimum of one Blank (BLK) per sample batch digested to determine if contamination or any memory effects are occurring. The BLK must be carried through all sample preparation steps. Results must be below the reporting limit.

18.5 Include a minimum of one Laboratory Control Sample (BS) per sample batch. The BS must be carried through all sample preparation steps. A BS is reagent water spiked with each element between the low and mid-level calibration range. Percent recovery is not to exceed 80%-120% recovery of the expected value. A laboratory-established control window may be used. If a BS is outside the control window, it must be re-run one time. If the re-analysis is outside the control window all samples associated with the BS must be re-prepared and re-analyzed.

18.6 Analyze one matrix spike (MS) and one matrix spike duplicate (MSD) at a frequency of at least 1 in 20 (5%). MS/MSDs are sample aliquots to which is added a known analyte concentration between the low and mid-level calibration range. Calculate percent recovery for each element. Percent recovery is not to exceed 75%-125% recovery (or a laboratory-established control window) with an RPD <20%. Matrix spiking monitors sample preparation efficiency relative to each matrix type. Relative percent difference (RPD) is calculated from the MS/MSD duplication. The RPD value monitors precision within sample preparation and analysis.

18.6.1 Pretreated samples must be spiked before digestion begins.

18.6.2 Samples not requiring pretreatment are spiked before loading on the autosampler tray.

18.6.2.1 Two "spiking solutions" are used to perform matrix spikes. These solutions are stable, but due to high analyte concentrations are not compatible when mixed.

18.6.3 Calculate MS/MSD percent recovery as follows:

$$\%R = \frac{C_{Spike} - C_{Orig}}{\text{Spike Concentration}} \times 100$$

where:

%R	=	Spike recovery, in %
C_{Spike}	=	Concentration of the spiked sample
C_{Orig}	=	Concentration of the unspiked sample
Spike Concentration	=	Concentration of the element spiked into the sample

18.6.4 Calculate MS/MSD relative percent difference as follows,

$$\%RPD = \frac{C_{MSD} - C_{MS}}{(C_{MSD} + C_{MS})/2} \times 100$$

where:

%RPD	=	Relative percent difference between the MS and MSD
C_{MSD}	=	Concentration of the MSD as read from the instrument data printout
C_{MS}	=	Concentration of the MSD as read from the instrument data printout

18.6.5 A matrix spike must recover within 70-130% (or within a laboratory-established control window) of the expected value. Precision between two matrix spikes must be ≤20%. Refer to TriMatrix SOP GR-10-106 for corrective actions.

18.7 The following tests must be performed with each sample batch to ensure that neither positive nor negative interferences are affecting element measurement or distorting reported value accuracies.

18.7.1 Post Spike (PS): The same sample from which the MS/MSD aliquots were prepared must also be spiked with a Post Spike. An analyte spike between the low and mid-range of the calibration curve is added to a portion of prepared digestate or digestate dilution. The control window is 80%-120% of the expected value. If MS/MSD recovery is acceptable and the PS is unacceptable, a serial dilution must be performed on the sample. If MS/MSD recovery is unacceptable and PS recovery is unacceptable then a matrix effect is confirmed. An alternative test method should be considered.

18.7.2 Serial Dilution: A serial dilution must be performed on the same sample as the MS/MSD, if analyte concentration is ≥100 times the IDL. Analysis of a 1:5 dilution must agree within ±10% of the original determination. If not, a chemical or physical interference effect must be suspected. Use the method of standard additions to compensate for this effect.

18.7.3 The method of standard additions involves adding known concentrations of a standard to three digestate aliquots. The three results are then used to construct a linear regression curve. The curve is extrapolated to find the point where it crosses the x-axis. The value of this point is the analyte concentration in the sample.

18.7.4 To perform the method of standard additions, prepare three spikes at 50%, 100% and 150% of the concentration found in the processed sample.

18.7.5 Analyze the spikes and the non-spiked processed sample. Using the regression program located on the laboratory intranet library, plot absorbance against concentration to construct a regression curve. The extrapolated x-intercept of the regression curve is the analyte concentration in the sample. Refer to Attachment 23.9 for a plot example. For results to be valid, the following limitations must be taken into consideration:

18.7.5.1 The curve constructed must be linear, with a correlation coefficient of ≥0.995.

18.7.5.2 The chemical form of the analyte added must respond the same way as the analyte in the sample.

18.7.5.3 The interference effect must be constant over the working range of concern.

18.7.5.4 The signal must be corrected for any additive interference.

18.7.5.5 The method of standard additions must be performed on any TCLP sample whose spike recovery is less than 50% and with a concentration less than or equal to the regulatory limit. The method of standard additions is also required when a TCLP extract concentration is within 20% of the regulatory limit. TCLP regulatory limits are as follows:

Element	Regulatory Limit (mg/L)	Element	Regulatory Limit (mg/L)
Arsenic	5.0 mg/L	Lead	5.0 mg/L
Barium	100 mg/L	Selenium	1.0 mg/L
Cadmium	1.0 mg/L	Silver	8.0 mg/L
Chromium	5.0 mg/L	Zinc	500 mg/L
Copper	100 mg/L		

18.7.5.6 The method of standard additions does not detect coincidental spectral overlap. If overlap is suspected, use computer compensation, an alternative wavelength or comparison with an alternate method to determine and/or correct.

18.7.6 Duplicate Analysis (DUP): If specified for a project, a DUP is analyzed as a substitute for, or in addition to the MSD. A DUP is a second sample aliquot analyzed in the same way as the first. The acceptance limit for DUP RPD is ≤20%.

18.8 Verify instrument calibration by analyzing appropriate quality control verification standards as described in Section 14.0.

18.9 Internal standardization (IS) must be used in all analyses to correct for instrument drift and physical interferences. A minimum of five internal standards are used at all times. Recovery for each internal standard is 70-120% of the expected value.

18.9.1 If an internal standard has low recovery (<70%), do a 1:5 dilution of the sample or digestate and re-analyze. If internal standard recovery is below 70%, do another 1:5 dilution. Repeat until acceptable internal standard recovery is achieved.

18.9.2 If an internal standard recovery is high (>120%), the element may be present in the sample. Use an alternate internal standard.

18.9.3 All internal standards must be within 50 amu of the element of interest.

18.10 Linear range studies must be performed semi-annually or more frequently if specified by any project DQO, or when there is a significant change in instrument response.

18.10.1 To perform a linear range study, calibrate the instrument as for sample analysis.

18.10.2 Run successive standards at an increasingly higher concentration and calculate percent recovery for each element. Begin by running a 200 ug/L standard.

18.10.3 If percent recovery is acceptable (90%-110%) for the 200 ug/L standard, run a higher concentration. Continue until percent recovery is not acceptable then run a standard at a lower concentration but higher than the last acceptable standard to zero in on the maximum value in the linear range.

18.10.4 The highest concentration run with acceptable percent recovery is the linear range.

19.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

19.1 Before the analysis of any actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC). While IDCs are not instrument dependent, one is required on each instrument used in sample analysis, to demonstrate the instrument's ability to generate acceptable accuracy and precision. Annually, a Continuing Demonstration of Capability (CDC) is required.

19.1.1 Initial Demonstration of Capability

19.1.1.1 Spike four aliquots of metals reagent water with a second source standard so concentration is in the lower half of the calibration range.

19.1.1.2 Digest and analyze the four spikes as samples following every step in the procedures.

19.1.1.3 Input the four results to the IDC spreadsheet located on the laboratory intranet library to calculate average percent recovery and relative standard deviation. Average recovery must be within blank spike control limits. Relative standard deviation must be ≤20%.

19.1.1.4 If either criterion is not met, locate and correct the source of the problem and repeat the study successfully.

19.1.1.5 Repeated failure will confirm a general problem with the procedure and/or techniques used. If this occurs, locate and correct the source of the problem, revise the procedure and/or techniques uses then repeat the study successfully.

19.1.1.6 Samples may not be analyzed by any analyst or on any instrument until a successful demonstration of capability study has been completed.

19.1.2 A Continuing Demonstration of Capability (CDC) study must be performed annually by one of the following:

19.1.2.1 By repeating the IDC study.

19.1.2.2 By using four consecutively analyzed blank spikes (if a second source is used) obtained from routine sample analysis if run exclusively by the analyst.

19.1.2.3 By successfully analyzing a performance testing sample during the course of routine sample analysis if run exclusively by the analyst.

19.1.2.4 By using the last four of seven results from an MDL study if run exclusively by the analyst. ONLY the last four results may be used.

19.1.3 Submit copies of all successful demonstrations of capability spreadsheets to the quality assurance department for data and training documentation.

19.2 A Method Detection Limit Study must be performed annually in accordance with TriMatrix SOP GR-10-125.

20.0 POLLUTION PREVENTION

20.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

20.2 Never dispose of laboratory chemicals without first referencing appropriate written instructions of disposal for that particular material.

20.3 Conserve the use of chemicals.

20.4 Comply with all environmental laws associated with chemicals in the laboratory.

21.0 WASTE MANAGEMENT

21.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals. Material safety data sheets are located in the library on the laboratory intranet.

21.2 To minimize the environmental impact and costs associated with chemical disposal, order and use only the minimum amount of material required.

21.3 Follow all instructions in TriMatrix SOP GR-15-102 for laboratory waste disposal requirements.

22.0 REFERENCES

22.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846,* 3rd Edition, Draft Update IVA, May 1998, Method 6020A, "Inductively Coupled Plasma – Mass Spectrometry", Revision 1, January 1998

23.0 ATTACHMENTS

23.1 Instrument Maintenance Logbook Example

23.2 Standards Log Example

23.3 Preparation Batch Report Example

23.4 Data Review Report Example

23.5 Internal Chain-of-Custody Example

23.6 SCV Standard Solution

23.7 Element Conditions

23.8 Spiking Solution Final Concentration

23.9 MSA Curve Example

23.10 Ionic Interference Correction Report Example

Attachment 23.1
Instrument Maintenance Logbook Example

TriMatrix Laboratories, Inc.

ICP Instrument Maintenance Logbook

Date	Analyst	Changed Pump Tube	Torch		Nebulizer		Wavelength Calibration	Alumina Injector		Replaced RF Coil	Other/Comments
			Cleaned	Replaced	Cleaned	Changed Tips		Cleaned	Replaced		
2-6-01	KW										Changed cones
2/7/01	SCM	✓									-changed pump tube -changed mist-elim. filter
2/8/01	SCM	✓									
2/9/01	SCM	✓									changed cones.
2-12-01	KW	✓									
2/16/01	SCM	✓									
2/23/01	SCM	✓									changed cones
2-18-01	DWT	7:25 am									
2-19-01	DWT	7:45 am									
2-19-01	DWT										replaced cones
2-20-01	DSC	9:15 am									
2/21/01	SCM	8:30 am									
2/23/01	SCM	4:05 pm									changed cone
7-21-01	KW	8:00 am									

file: MaintICP.xls page: 2 of 50 revision: 1.0

Attachment 23.2
Standards Log Example

Analytical Standard Record
TriMatrix Laboratories, Inc.
A602735

Description:	QCA ICPMS	Expires:	Mar-31-07
Standard Type:	Analyte Spike	Prepared:	Mar-31-05
Solvent:	Solvent Lot #605319	Prepared By:	** Vendor **
Final Volume (mls):	1000	Department:	Expired
Vials:	1	Last Edit:	Jan-30-07 13:48 by DSC

Environmental Express part# EP20-9-1-IL Solution A
Lot 605319
Received 2-28-06

Analyte	CAS Number	Concentration	Units
Aluminum	7429-90-5	100	mg/L
Arsenic	7440-38-2	100	mg/L
Arsenic, OWEP-SAR	7440-38-2	100	mg/L
Arsenic, OWEP-TAR	7440-38-2	100	mg/L
Barium	7440-39-3	100	mg/L
Beryllium	7440-41-7	100	mg/L
Boron	7440-42-8	100	mg/L
Cadmium	7440-43-9	100	mg/L
Calcium	7440-70-2	1000	mg/L
Chromium	7440-47-3	100	mg/L
Cobalt	7440-48-4	100	mg/L
Copper	7440-50-8	100	mg/L
Iron	7439-89-6	100	mg/L
Lead	7439-92-1	100	mg/L
Lead, Total (Coarse)	7439-92-1	100	mg/L
Lead, Total (Fine)	7439-92-1	100	mg/L
Lithium	7439-93-2	100	mg/L
Magnesium	7439-95-4	1000	mg/L
Manganese	7439-96-5	100	mg/L
Nickel	7440-02-0	100	mg/L
Phosphorus	7723-14-0	100	mg/L
Potassium	7440-09-7	1000	mg/L
Selenium	7782-49-2	100	mg/L
Selenium, OWEP-SAR	7782-49-2	100	mg/L
Selenium, OWEP-TAR	7782-49-2	100	mg/L
Silver	7440-22-4	100	mg/L
Sodium	7440-23-5	1000	mg/L
Strontium	7440-24-6	100	mg/L
Thallium	7440-28-0	100	mg/L
Thallium, OWEP-SAR	7440-28-0	100	mg/L

Reviewed By: Date:

Page 1 of 2

Analytical Standard Record
TriMatrix Laboratories, Inc.
A602735

Thallium, OWEP-TAR	7440-28-0	100	mg/L
Vanadium	7440-62-2	100	mg/L
Zinc	7440-66-6	100	mg/L

Reviewed By: Date:

Page 2 of 2

Approved By: 1-15-09 **Approved By:** 1-19-09
QA Officer **Area Supervisor**

Attachment 23.3
Preparation Batch Report Example

TriMatrix Laboratories, Inc. **PREPARATION BATCH** 0609650 Page 1 of 2 Printed: 10/5/2007 3:04:45PM

Metals, Water, 3020A Digestion
(No Surrogate)
Batch Comments: 08/23/06 6:15am-2:30pm

Work Order	Analysis	Work Order	Analysis	Work Order	Analysis
0608312	Se Total 6020	0608312	Pb Total 6020	0608312	Cr Total 6020
0608312	Cd Total 6020	0608312	As Total 6020	0608312	Ag Total 6020
0608355	Zn Total 6020	0608355	Se Total 6020	0608355	Pb Total 6020
0608355	Cu Total 6020	0608355	Cr Total 6020	0608355	Cd Total 6020
0608355	Ba Total 6020	0608355	As Total 6020	0608355	Ag Total 6020

Lab Number	Contain	Prepared	By	Initial (mL)	Final (mL)	uL Surrogate	Source ID	Spike ID	uL Spike	Client/ QC Type	Extraction Comments
0609650-BLK1		Aug-23-06 06:15	LMA	25	125					BLANK	
0609650-BS1		Aug-23-06 06:15	LMA	25	125			A602735	25	LCS	
0609650-MS1		Aug-23-06 06:15	LMA	25	125		0608355-22	A602735	25	MATRIX SPIKE	
0609650-MSD1		Aug-23-06 06:15	LMA	25	125		0608355-22	A602735	25	MATRIX SPIKE DUP	
0608312-23	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608312-23	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608312-23	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608312-23	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608312-23	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608312-23	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-21	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-21	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-21	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-21	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-21	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-21	A	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-22	C	Aug-23-06 06:15		25	125					[redacted]	Added for Sequence QC in 6092623
0608355-22	C	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-22	C	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-22	C	Aug-23-06 06:15	LMA	25	125					[redacted]	

Comments | Analyst Initials

bch_TriMatrix.rpt

TriMatrix Laboratories, Inc. **PREPARATION BATCH** 0609650 Page 2 of 2 Printed: 10/5/2007 3:04:45PM

Metals, Water, 3020A Digestion
(No Surrogate)
Batch Comments: 08/23/06 6:15am-2:30pm

Lab Number	Contain	Prepared	By	Initial (mL)	Final (mL)	uL Surrogate	Source ID	Spike ID	uL Spike	Client/ QC Type	Extraction Comments
0608355-22	C	Aug-23-06 06:15		25	125					[redacted]	Added for Sequence QC in 6092623
0608355-22	C	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-22	C	Aug-23-06 06:15	LMA	25	125					[redacted]	
0608355-22	C	Aug-23-06 06:15		25	125					[redacted]	Added for Sequence QC in 6092623
0608355-22	C	Aug-23-06 06:15	LMA	25	125					[redacted]	
0609650-PS1		Aug-28-06 13:15	DSC	2	10		0608355-22	A603196	50	POST SPIKE	[Spk] 25mL->125mL; 10mL->10mL; Spi
0609650-PS2		Aug-28-06 14:00	DSC	2	10		0608355-22	A603196	100	POST SPIKE	[Spk] 25mL->125mL; 10mL->10mL; Spi

Comments | Analyst Initials

bch_TriMatrix.rpt

Approved By: 1-15-09 **QA Officer**

Approved By: 1-19-09 **Area Supervisor**

Attachment 23.4
Data Review Report Example

TriMatrix Laboratories, Inc

Data Review Report – Metals Lab
Sequence = 6090602 Page 1 of 4

SampleID	Analysis	IResult	Qualifier	IUnits	Dilu	FResult	FUnits	IMDL	IMRL	FM
6090602-CAL1	Ag Total 6020	0		ug/L	1	0.00	ug/L	0.024	0.04	
6090602-CAL1	Cu Total 6020	0		ug/L	1	0.00	ug/L	0.066	0.2	
6090602-CAL1	Pb Total 6020	0		ug/L	1	0.00	ug/L	0.065	0.2	
6090602-CAL1	Tl Total 6020	0		ug/L	1	0.00	ug/L	0.034	0.2	
6090602-CAL1	V Total 6020	0		ug/L	1	0.00	ug/L	0.17	0.2	
6090602-CAL2	Ag Total 6020	0.04		ug/L	1	0.0400	ug/L	0.024	0.04	
6090602-CAL3	Ag Total 6020	0.200592		ug/L	1	0.201	ug/L	0.024	0.04	
6090602-CAL3	Cu Total 6020	0.2		ug/L	1	0.200	ug/L	0.066	0.2	
6090602-CAL3	Pb Total 6020	0.2		ug/L	1	0.200	ug/L	0.065	0.2	
6090602-CAL3	Tl Total 6020	0.2		ug/L	1	0.200	ug/L	0.034	0.2	
6090602-CAL3	V Total 6020	0.2		ug/L	1	0.200	ug/L	0.17	0.2	
6090602-CAL4	Ag Total 6020	1.000291		ug/L	1	1.00	ug/L	0.024	0.04	
6090602-CAL4	Cu Total 6020	1.002342		ug/L	1	1.00	ug/L	0.066	0.2	
6090602-CAL4	Pb Total 6020	1.00034		ug/L	1	1.00	ug/L	0.065	0.2	
6090602-CAL4	Tl Total 6020	1.000458		ug/L	1	1.00	ug/L	0.034	0.2	
6090602-CAL4	V Total 6020	0.99989		ug/L	1	1.00	ug/L	0.17	0.2	
6090602-CAL5	Ag Total 6020	9.985816		ug/L	1	9.99	ug/L	0.024	0.04	
6090602-CAL5	Cu Total 6020	9.987423		ug/L	1	9.99	ug/L	0.066	0.2	
6090602-CAL5	Pb Total 6020	9.989133		ug/L	1	9.99	ug/L	0.065	0.2	
6090602-CAL5	Tl Total 6020	9.987994		ug/L	1	9.99	ug/L	0.034	0.2	
6090602-CAL5	V Total 6020	9.989468		ug/L	1	9.99	ug/L	0.17	0.2	
6090602-CAL6	Ag Total 6020	20.23713		ug/L	1	20.2	ug/L	0.024	0.04	
6090602-CAL6	Cu Total 6020	20.21078		ug/L	1	20.2	ug/L	0.066	0.2	
6090602-CAL6	Pb Total 6020	20.06989		ug/L	1	20.1	ug/L	0.065	0.2	
6090602-CAL6	Tl Total 6020	20.14292		ug/L	1	20.1	ug/L	0.034	0.2	
6090602-CAL6	V Total 6020	20.06358		ug/L	1	20.1	ug/L	0.17	0.2	
6090602-CAL7	Ag Total 6020	49.5229		ug/L	1	49.5	ug/L	0.024	0.04	
6090602-CAL7	Cu Total 6020	49.47732		ug/L	1	49.5	ug/L	0.066	0.2	
6090602-CAL7	Pb Total 6020	49.94873		ug/L	1	49.9	ug/L	0.065	0.2	
6090602-CAL7	Tl Total 6020	49.54875		ug/L	1	49.5	ug/L	0.034	0.2	
6090602-CAL7	V Total 6020	49.59988		ug/L	1	49.6	ug/L	0.17	0.2	
6090602-CAL8	Pb Total 6020	101.319		ug/L	1	101	ug/L	0.065	0.2	
6090602-ICV1	Ag Total 6020	42.35505		ug/L	1	42.4	ug/L	0.024	0.04	
6090602-ICV1	Cu Total 6020	42.45268		ug/L	1	42.5	ug/L	0.066	0.2	
6090602-ICV1	Pb Total 6020	41.42369		ug/L	1	41.4	ug/L	0.065	0.2	
6090602-ICV1	Tl Total 6020	43.27606		ug/L	1	43.3	ug/L	0.034	0.2	
6090602-ICV1	V Total 6020	40.95888		ug/L	1	41.0	ug/L	0.17	0.2	
6090602-SCV1	Ag Total 6020	42.35505		ug/L	1	42.4	ug/L	0.024	0.04	
6090602-SCV1	Cu Total 6020	42.45268		ug/L	1	42.5	ug/L	0.066	0.2	
6090602-SCV1	Pb Total 6020	41.42369		ug/L	1	41.4	ug/L	0.065	0.2	
6090602-SCV1	Tl Total 6020	43.27606		ug/L	1	43.3	ug/L	0.034	0.2	
6090602-SCV1	V Total 6020	40.95888		ug/L	1	41.0	ug/L	0.17	0.2	
6090602-ICB1	Ag Total 6020	0.009662		ug/L	1	0.00966	ug/L	0.024	0.04	
6090602-ICB1	Cu Total 6020	0.004933		ug/L	1	0.00493	ug/L	0.066	0.2	
6090602-ICB1	Pb Total 6020	0.003587		ug/L	1	0.00359	ug/L	0.065	0.2	
6090602-ICB1	Tl Total 6020	0.004911		ug/L	1	0.00491	ug/L	0.034	0.2	
6090602-ICB1	V Total 6020	0.016471		ug/L	1	0.0165	ug/L	0.17	0.2	
6090602-CRL1	Ag Total 6020	0.224835		ug/L	1	0.225	ug/L	0.024	0.04	
6090602-CRL2	Cu Total 6020	1.146779		ug/L	1	1.15	ug/L	0.066	0.2	

TriMatrix Laboratories, Inc

Data Review Report -- Metals Lab
Sequence = 6090602 Page 4 of 4

SampleID	Analysis	IResult	Qualifier	IUnits	Dilu	FResult	FUnits	IMDL	IMRL	FMR
0608367-02	Cu Total 6020	2.761238	ME004	ug/L	1	14	ug/L	0.322	4	4
0608367-02	Ag Total 6020	0.020862		ug/L	1	0.10	ug/L	0.0726	0.2	0.2
0608367-03	V Total 6020	0.947256		ug/L	1	4.7	ug/L	0.259	4	4
0608367-03	Cu Total 6020	0.817287		ug/L	1	4.1	ug/L	0.322	4	4
0608367-03	Ag Total 6020	0.010797		ug/L	1	0.054	ug/L	0.0726	0.2	0.2
6090602-CCV4	Ag Total 6020	43.3769		ug/L	1	43.4	ug/L	0.024	0.04	
6090602-CCV4	Cu Total 6020	43.01479		ug/L	1	43.0	ug/L	0.066	0.2	
6090602-CCV4	V Total 6020	42.85077		ug/L	1	42.9	ug/L	0.17	0.2	
6090602-CCB4	Ag Total 6020	0.007124		ug/L	1	0.00712	ug/L	0.024	0.04	
6090602-CCB4	Cu Total 6020	0.007699		ug/L	1	0.00790	ug/L	0.066	0.2	
6090602-CCB4	V Total 6020	0.009801		ug/L	1	0.00980	ug/L	0.17	0.2	

Approved By: MD 1-15-09 **Approved By:** DA 1-29-09
QA Officer **Area Supervisor**

Attachment 23.5
Internal Chain Of Custody Example

24-JUL-2000 TRIMATRIX LABORATORIES, INC. PAGE N19

CHAIN OF CUSTODY REPORT FOR AN ENTIRE SUBMITTAL

CLIENT: [redacted] PROJECT: [redacted]

SUBMITTAL: Sampling Event #1 PROJECT: 35465-1

Parameter: ~~ARSENIC, TOTAL~~ All Metals Method: MS/EPA/WT Ref Cit: EPA-200.8/6020 Matrix: WATER

SAMPLE #	REMOVED BY: (SIGNATURE)	DATE & TIME REMOVED	RELINQUISHED BY: DATE & TIME	RECEIVED BY: DATE & TIME	DATE & TIME RETURNED
253868	Denise Coffey			7-21-00	7-28-00
253869					
253870					
253871					
253872					DSC
253873				DSC	
253874					
253875					
253876	DSC				
253877					
253878					
253879					
253880					
253881					
253882					
253883	Denise Coffey			7-21-00	7-28-00

Attachment 23.6
SCV Standard Solution

Element	Concentration (mg/L)	Diluted Concentration (ug/L)
Aluminum	10	40
Antimony	10	40
Arsenic	10	40
Barium	10	40
Beryllium	10	40
Boron	10	40
Cadmium	10	40
Chromium	10	40
Cobalt	10	40
Copper	10	40
Lead	10	40
Manganese	10	40
Molybdenum	10	40
Nickel	10	40
Selenium	10	40
Silver	10	40
Thallium	10	40
Tin	10	40
Vanadium	10	40
Zinc	10	40
Uranium	10	40
Strontium	10	40

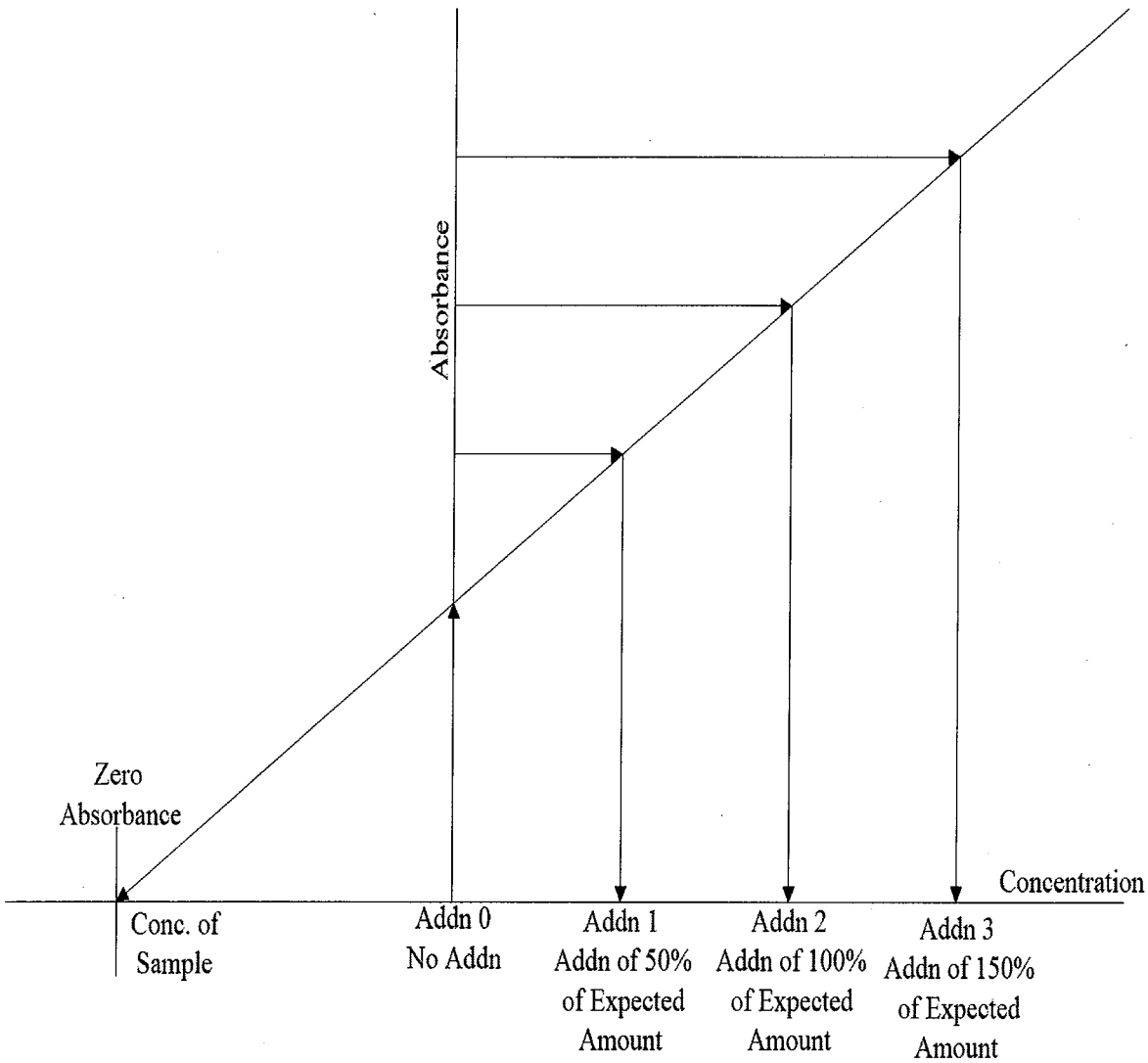
Attachment 23.7
Element Conditions

Int Std	Analyte	Mass [amu]	Scan Mode	MCA Channels	Dwell Time per AMU [ms]	Integration Time [ms]	Corrections
Li		6.0151	Peak Hopping	1	100	1000	
	Be	9.0122	Peak Hopping	1	100	1000	
		44.9559	Peak Hopping	1	100	1000	
	V	50.944	Peak Hopping	1	100	1000	C10, Cr
	Cr	52.9407	Peak Hopping	1	100	1000	
	Mn	51.9405	Peak Hopping	1	100	1000	
	Co	58.9332	Peak Hopping	1	100	1000	
	+Ni	59.9332	Peak Hopping	1	100	1000	
	Ni	60.931	Peak Hopping	1	100	1000	
	+Cu	62.9298	Peak Hopping	1	100	1000	
	Cu	64.9278	Peak Hopping	1	100	1000	
	+Zn	65.926	Peak Hopping	1	100	1000	
	Zn	66.9271	Peak Hopping	1	100	1000	
	Zn	67.9249	Peak Hopping	1	100	1000	
	As	74.9216	Peak Hopping	1	100	1000	ArCl, Se
	Se	81.9767	Peak Hopping	1	100	1000	
Ge		88.9054	Peak Hopping	1	100	1000	
	Mo	97.9055	Peak Hopping	1	100	1000	Ru
	+Ag	106.905	Peak Hopping	1	100	1000	
	Ag	108.905	Peak Hopping	1	100	1000	
	+Cd	110.904	Peak Hopping	1	100	1000	Mo, Pd
	Cd	113.904	Peak Hopping	1	100	1000	Sn
In		114.904	Peak Hopping	1	100	1000	Sn
	Sb	120.904	Peak Hopping	1	100	1000	
	+Sb	122.904	Peak Hopping	1	100	1000	Te
	Ba	134.906	Peak Hopping	1	100	1000	
	+Ba	136.905	Peak Hopping	1	100	1000	
Tb		158.925	Peak Hopping	1	100	1000	
	Tl	202.972	Peak Hopping	1	100	1000	
	+Tl	204.975	Peak Hopping	1	100	1000	
	Pb	207.977	Peak Hopping	1	100	1000	Pb, Pb
Bi		208.980	Peak Hopping	1	100	1000	

Attachment 23.8
Spiking Solutions Final Concentrations

Element	Aqueous Samples (ug/L)	Solid Samples (mg/kg)
Aluminum	50	20
Antimony	50	20
Arsenic	50	20
Barium	50	20
Beryllium	50	20
Boron	50	20
Cadmium	50	20
Chromium	50	20
Cobalt	50	20
Copper	50	20
Lead	50	20
Manganese	50	20
Molybdenum	50	20
Nickel	50	20
Selenium	50	20
Silver	50	20
Thallium	50	20
Tin	50	20
Vanadium	50	20
Zinc	50	20

Attachment 23.9
MSA Curve Example



Attachment 23.10
Ionic Interference Correction Report Example

Quantitative Analysis Calibration Report

File Name:
File Path:
Calibration Type: External Calibration

Analyte	Mass	Curve Type	Slope	Intercept	Corr. Coeff.

Method Equation

Analyte	Mass	Corrections
V	50.944	-2.706684618 *(ClO 53 -(0.393948145 *Cr 52))
As	74.922	-2.706684618 *(ArCl 77 -(1.549850256 *Se 82))
Se	81.917	- 1.007833 *Kr 83
Mo	97.906	- 0.109613 *Ru 101
Cd	110.904	-0.909241101 *(MoO 108 -(0.712*Pd 106))
Cd	113.904	- 0.027250 * Sn 118
In	114.904	- 0.014038 * Sn 118
Sn	119.902	- 0.012730 * Te 125
Sb	122.904	- 0.125884 * Te 125
Pb	207.977	+1*Pb 206 +1*Pb 207

Approved By: 1-15-09 **Approved By:** DSC 1-19-09
QA Officer **Area Supervisor**

TriMatrix Laboratories, Inc.

UNCONTROLLED COPY

STANDARD OPERATING PROCEDURE

Mercury by semi-Automated Cold Vapor Atomic Absorption

EPA Method 245.1
SW-846 Method 7470A
SW-846 Method 7471A

APPROVALS:

Area Supervisor: Denise S. Coffey Date: 1-19-09

QA Officer: Tom C. Boocher Date: 1-15-09

Operations Manager: Jeff P. Glaser Date: 1/19/09

Procedure Number: GR-01-123
Revision Number: 5.6

Date Initiated: 5/6/93
Effective Date: 2/1/09

Date Revised: 1/15/09
Pages Revised: All

By: David W. Johnson
Total Number of Pages: 21

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

1.0 SCOPE AND APPLICATION

1.1 This procedure includes analysis for total mercury (inorganic/organic) in mobility extracts, aqueous wastes, groundwaters, drinking waters, surface waters, saline waters, wastewaters, domestic industrial wastes, soils, wastes, sludges and oils. All samples must undergo a preliminary digestion.

1.2 The typical reporting limit is 0.2 ug/L mercury for aqueous and 0.10 mg/kg for solid sample matrices.

2.0 PRINCIPAL METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 1, September 1994, Method 7470A, "Mercury in Liquid Waste (Manual Cold-Vapor Technique)"

2.2 *Methods for the Determination of Metals in Environmental Samples,* Supplement I, May 1994, Revision 5.4, EMMC Version, "Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry", Method 245.1, Revision 3.0, May, 1994

2.3 *Test Method for Evaluating Solid Waste, Physical/Chemical Methods,* SW-846, 3rd Edition, Final Update III, Revision I, September 1994, Method 7471A, *"Mercury in Solid and Semi Solid Waste* (Manual Cold-Vapor Technique)"

3.0 SUMMARY OF PROCEDURE

3.1 Before analysis, all analytical and quality control samples must be pretreated according to the references discussed in Section 5.0. These digestions reduce organo-mercury compounds to inorganic mercury. Inorganic mercury is then converted to mercury in the Hg^{2+} state. All Hg^{2+} with an HCl carrier enters a gas liquid separatory where it is mixed with stannous chloride to form elemental mercury vapor (Hg^0) according to the following equation:

$$Hg^{2+} + Sn^{2+} \rightarrow Hg^0 + Sn^{4+}$$

3.2 The mixture then flows into a liquid-gas separator where argon is introduced to carry the mercury vapor through a drying tube. The dried mercury vapor then enters one path of a heated double-path optical cell that has been optimized for fast response time. A mercury source powered by a constant current power supply delivers a stable source of absorbance at 253.7 nm. Absorbance by the mercury vapor is measured using a solid-state detector with a wide dynamic range. The resulting signal is referenced to the simultaneous absorbance of the pure carrier gas flowing through the second optical path under identical conditions.

3.3 Absorbance of standards is plotted against known concentrations to build a calibration curve. Absorbance of unknown samples are read against the calibration curve, and regressed to concentration in ug/L. The mercury vapor is vented up a hood to minimize contamination of other samples.

4.0 PARAMETER OR COMPOUND LIST

4.1 Mercury

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal*, latest revision

5.2 TriMatrix SOP GR-01-140, *Preparation Procedure for Mercury in Water, Wastewater, and Liquid Wastes,* latest revision

5.3 TriMatrix SOP GR-01-139, *Preparation Procedure for Mercury in Soils, Wastes, and Oils,* latest revision

5.4 TriMatrix SOP GR-10-106, Inorganic *and Metals Laboratories Corrective Actions,* latest revision.

5.5 TriMatrix SOP GR-10-123, *Element Data Transfer and Review*, latest revision

5.6 TriMatrix SOP GR-10-111, *Micropipette/Macropipette Calibration and Verification*, latest revision

5.7 TriMatrix SOP GR-10-125, *Method Detection Limit (MDL)*, latest revision

5.8 TriMatrix SOP GR-09-128, Homogenization, Grinding and Drying of Solid Samples, latest revision

5.9 *PSA 10.045 Millenium Merlin/Galahad System User Manual,* Issue Number 1.1, Issue Date July 10, 1999

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Soil samples often contain mercury at low levels. When soils are mixed and ground, there exists the possibility that liquid samples may become contaminated by dust from the air. Therefore, preparation areas for mercury must be kept free of dust and dirt.

Note: Mixing and grinding samples must be done in a fume hood for safety.

6.2 If a mercury thermometer is broken anywhere in the laboratory, notify the metals laboratory so precautionary measures against contamination can be taken.

6.3 Mercury may be lost if the digestion temperature goes above 95° C. The digestion temperature must be monitored and recorded with a digital thermometer on the digestion benchsheet.

6.4 Reagents used may become contaminated over time. If contamination is suspected, the reagent must be discarded following proper laboratory disposal guidelines and fresh reagent made.

6.5 Potassium permanganate is added to eliminate possible interference from sulfide as sodium sulfide.

6.6 Copper interferes at concentrations above 10 mg/L.

6.7 Samples high in chlorides and volatile organic materials require additional permanganate.

Note: The maximum permanganate added to a sample in the digestion batch must be added to all associated quality control samples.

7.0 SAFETY PRECAUTIONS

7.1 Comply with all instructions for health and safety as outlined in the TriMatrix laboratory safety manual and chemical hygiene plan.

7.2 Concentrated acids are used. Disposable gloves, safety glasses and a laboratory coat must be worn at all times when handling concentrated acids. Gloves, safety glasses and laboratory coats must also be worn when handling digested samples or performing any work within the metals laboratory. Refer to the MSDS located on the library drive for information on any chemical used.

7.3 Make sure the venting system is hooked up and running. Do not operate the instrument if it is not properly ventilated.

7.4 Mercury lamps emit UV radiation. Avoid looking directly at the lamp without some type of strong UV protection. Failure to follow this policy may cause very serious and immediate damage to the retina of the eye.

7.5 Mercury exists in many forms and is toxic in a variety of ways. Mercury vapor is toxic if inhaled. Mercury compounds can also be absorbed through the skin. Wear disposable gloves at all times. Elemental Hg^0 and Hg^{2+} are toxic if ingested. Always wash hands after handling mercury standards, samples or reagents, and when leaving the laboratory.

7.6 No food or drink is allowed in the metals laboratory. Food and drink may be consumed in the laboratory office but not stored there.

7.7 Wash hands before starting work. Chemicals may be present on the skin that can interfere with mercury analysis. Wash hands before leaving the laboratory. Chemicals and acids may be on the skin that could eventually be ingested or passed on to a third party through casual contact.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Samples should be acidified at the time of collection to a pH of <2. If the pH is not <2 when received by the laboratory, lower to pH <2 during the sample receipt process. A minimum of 24 hours must elapse after pH adjustment by the laboratory before performing the sample digestion.

8.2 Store non-aqueous and solid samples at 4 ±2° C.

8.3 The maximum holding time for all mercury samples is 28 days from the collection date. Analyze non-aqueous samples as soon as possible within that time.

8.4 All samples must be subjected to digestion before analysis.

8.5 The minimum collected aqueous sample volume required is 100 mL. If quality control is also required, collect at least 300 mL. The minimum sample size for solid samples is 10 g.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Laboratory analytical balance capable of weighing 0.0001 g

9.2 Laboratory balance capable of weighing 0.1 g

9.3 Macropipettor capable of delivering 50 - 1000 µL

9.4 Class A volumetric flasks, various volumes

9.5 Class A reusable pipettes, various volumes

9.6 Macropipettes capable of delivering 5 - 10 mL of solution

9.7 Wooden laboratory spatulas

9.8 Calibrated digital thermometer capable of reading to 100° C. Mercury thermometers must never be used in this procedure.

9.9 PSA low-level absorbance mercury analyzer, Millenium system, model 10.045

9.10 Computer running Avalon software. An IBM compatible computer running Windows NT 4.0 service pack 5.0. The software version may be updated without notice if it performs at least as well as the older version.

9.11 Filter, 0.45 µm glass fiber.

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Check the calibration on autopipettors daily. Remove from service and send out for recertification when daily checks indicate unacceptable accuracy or performance. Perform an annual inspection to determine overall condition.

10.2 Verify balance calibration daily. Remove from service and call for repair when daily checks indicate unacceptable accuracy or performance. Recertify annually through a contracted service representative.

10.3 Inspect the waste bottle under the instrument before starting. If the bottle is full, properly dispose of the liquid.

10.4 Under normal conditions, the PSA requires very little maintenance. However, attention to the maintenance schedule below must be followed:

10.4.1 Daily:

10.4.1.1 Before shutting down, flush all tubing and the sample valve with laboratory reagent water. Finally, flush with air.

10.4.1.2 It may necessary to replace all tubing. However, flushing of the sample valve must still take place.

10.4.1.3 Replace the pump tubing if required. When in doubt, replace it.

10.4.1.4 Ensure that glassware is clean. When in doubt, clean it.

10.4.1.5 Clean all outer surfaces of the instrument.

10.4.1.6 Also after shutting down, release any tension on the pump tubing.

10.4.2 Weekly:

10.4.2.1 Perform daily maintenance activities.

10.4.2.2 Replace all pump tubing if not already replaced as part of the daily maintenance.

10.4.3 Monthly:

10.4.3.1 Perform daily and weekly maintenance activities.

10.4.3.2 Replace all pump tubing if not already replaced as part of daily/weekly maintenance.

10.4.3.3 Check for discoloration in the Perma-pure drying system and replace as necessary.

10.4.4 Six Months:

10.4.4.1 Perform daily, weekly and monthly maintenance.

10.4.4.2 Replace the inner membrane of the Perma-pure drying system if needed.

10.4.5 Yearly:

10.4.5.1 Perform daily, weekly, monthly and six month maintenance.

10.4.5.2 Change the inner membrane of the Perma-pure drying system if needed.

10.4.5.3 Replace the activated charcoal in the exhaust line.

10.4.6 Cleaning:

10.4.6.1 Before undertaking any cleaning, disconnect the main supply cable from the instrument. Cleaning is ONLY recommended for the outer case.

10.4.6.2 Clean with a damp cloth or sponge which has been previously immersed in warm soapy water. Alternatively, a suitable laboratory cleaning agent may be used. Avoid copious amounts of liquid coming into contact with the instrument.

10.4.6.3 Finish off by wiping down with a dry lint-free cloth or sponge.

10.4.7 Wipe acid spills up with a suitable neutralizing agent IMMEDIATELY. However, be careful to avoid a copious volume of liquid coming into contact with the instrument.

11.0 CHEMICALS AND REAGENTS

11.1 Acids used in standards preparation and for samples must be trace metal grade or better.

11.1.1 Concentrated hydrochloric acid, trace metal grade

11.1.2 Concentrated nitric acid, trace metal grade

11.2 ASTM Type II water

11.2.1 Deionized water is fed into an all-glass distillation unit. The resulting distillate is immediately placed into a plastic container. This is the only water acceptable for mercury analysis.

11.3 Argon gas supply

11.3.1 Welding grade or better. This is plumbed from a liquid argon tank located outside the building. Argon is used as the carrier gas during analysis.

11.4 Stannous chloride, 2% solution in 10% hydrochloric Acid.

11.4.1 Place 20 g stannous chloride into a clean 1 L polyethylene bottle. Add 100 mL concentrated HCl and swirl until the SnCl is dissolved. Add 880 mL ASTM Type II water then cap and mix.

11.4.2 Create a new standard number in Element™ when the stannous chloride lot changes.

12.0 STANDARDS PREPARATION

12.1 Refer to TriMatrix SOP GR-01-139 and SOP GR-01-140, for the preparation of mercury standards.

13.0 SAMPLE PREPARATION

13.1 Refer to TriMatrix SOP GR-01-139 and SOP GR-01-140 for the preparation of samples by matrix.

14.0 CALIBRATION PROCEDURES

14.1 A blank and five standards comprise the initial calibration curve. Refer to TriMatrix SOP GR-01-139 and SOP GR-01-140 for the preparation of calibration standards.

14.2 Prepare a digested calibration curve the same day as digestates and use for quantitation.

15.0 ANALYTICAL PROCEDURE

15.1 Analysts must be familiar with the software's operation by reading the software manual and through documented training from an experienced analyst before proceeding.

15.2 After running the calibration curve, analyze a second-source calibration verification (SCV) as a sample. The SCV is prepared from a second-source purchased standard and prepared at 3.0 ug/L. SCV recovery must be within 95 – 105% of the expected value for method reference 245.1 or within 90 – 110% for method references 7470A and 7471A.

15.2.1 If the SCV fails recovery, repeat the analysis.

15.2.2 If the second analysis fails, initiate corrective action:

15.2.2.1 Adjust the gas flow if needed.

15.2.2.2 Replace tubing if needed.

15.2.2.3 Check for other mechanical problems to verify the instrument is operating correctly.

15.2.3.4 Remake and redigest the calibration standards if necessary.

15.2.3.5 Remake the SCV standard if necessary.

15.2.3 After resolving the problem, recalibrate the instrument and run the SCV successfully.

15.2.4 Digestions may not be analyzed without an acceptable SCV.

15.3 Analyze a calibration blank (CCB) after the SCV. The mercury concentration found in the CCB must not be greater than the absolute value of the reporting limit to be acceptable.

15.4.1 If the CCB is higher than the reporting limit, reanalyze one time.

15.4.2 If the second analysis fails, initiate corrective action.

15.4.2.1 Locate the source of the contamination.

15.4.2.2 Correct the contamination problem.

15.4.2.3 Repeat all associated sample digestions associated with the contamination problem and/or narrate the contamination.

15.5 Analyze a contract-required limit (CRL) standard at the beginning of each run.

15.5.1 A CRL is reanalysis of the digested 0.2 ug/L standard from the initial calibration curve as a sample.

15.5.2 CRL recovery must fall within 50 – 150% of the expected value. If the CRL result is above the calculated MDL value but outside the control limits, narrate in the analytical batch as follows:

15.5.2.1 The CRL recovery for this analyte was outside laboratory control limits. However, the only requirement is that the analyte be detected. No qualifications are necessary.

15.6 After analysis of the CRL, analyze a continuing calibration verification (CCV) standard. The CCV is the midpoint calibration standard analyzed as a sample. CCV recovery must be within 90 – 110% of the expected value.

15.6.1 If the CCV fails, reanalyze one time.

15.6.2 If the CCV still fails, stop the analysis and initiate corrective action.

15.6.2.1 Check to make sure the instrument is operating correctly.

15.6.2.2 Recalibrate.

15.6.2.3 Reanalyze all digestates since the last acceptable CCV.

15.7 Analyze a continuing calibration blank (CCB). The mercury concentration found in the CCB must not be greater than the absolute value of the reporting limit to be acceptable.

15.7.1 If the CCB fails, reanalyze one time.

15.7.2 If the second analysis fails, initiate corrective action:

15.7.2.1 If a high level sample is carrying over, analyze the CCB until the system is clean then reanalyze all digestates run since the last acceptable CCB.

15.7.2.2 If no apparent cause can be found, recalibrate then reanalyze all digestates run since the last acceptable CCB.

15.8 After the initial quality control has passed, analyze up to 10 samples (including the high and low concentration blank spikes) then repeat analysis of the CCV and CCB. Repeat, until all samples are analyzed.

Note: Shake all digestates before analysis. Solid matrix digestates must be filtered through a 0.45 µm filter before analysis.

15.9 Check all raw data to make sure each result is within the calibration range. If any result above the calibration range, mark the sample number and estimate a dilution factor. Make the dilution using a digestion CCB that matches the sample reagent matrix then analyze within the calibration range.

15.9 Verify the calibration after all samples have been analyzed as follows:

15.9.1 Analyze a final CCV successfully.

15.9.2 Analyze a final CCB successfully, which concludes the run.

16.0 CALCULATIONS AND DATA HANDLING

16.1 Sample concentration is read directly from the computer printout in ug/L. Dilution factors must be taken into account in the ID/WT file and the sample information file.

16.1.1 Quantitate water, wastewater and potable water samples as follows:

$$C_{Final} = C_{Instr} \times DF_{Subseq}$$

where:

C_{Final} = The final reported concentration in ug/L
C_{Instr} = The concentration as read from the instrument printout in ug/L
DF_{Subseq} = Any dilution ratio subsequent to the digestion dilution

16.1.2 Quantitate TCLP and SPLP leachates as follows:

$$C_{Final} = \left(\frac{C_{Inst} \text{ X } DF_{subsequent}}{1000}\right)$$

Where:

C_{Final} = The final reported concentration in mg/L
C_{Inst} = The concentration as read from the instrument printout in ug/L
$DF_{subsequent}$ = Any dilution ratio subsequent to the digestion dilution
1000 = Conversion from ug/L to mg/L

16.1.3 Quantitate solid samples as follows:

$$C_{Final} = \left(\frac{C_{Inst} \text{ X } DF_{subsequent}}{1000}\right)$$

Where:

C_{Final} = The final reported concentration in mg/kg
C_{Inst} = The concentration as read from the instrument printout in ug/kg
$DF_{subsequent}$ = Any dilution ratio subsequent to the digestion dilution
1000 = Conversion from ug/kg to mg/kg

16.2 Duplicate measurements are taken and recorded for each sample. The average of these two readings is reported as the final result.

17.0 DATA REPORTING AND DELIVERABLES

17.1 Analysts running samples are responsible for correctly filling in, handing in and filing all associated paperwork. It is essential to perform these tasks for the laboratory to provide clients with defensible data.

17.2 LIMS Reporting

17.2.1 When finished running a sample set, all data must be uploaded to Element™, the Laboratory Information Management System (LIMS) in accordance with TriMatrix SOP GR-10-123.

17.2.1.1 To export a data set from the instrument for LIMS uploading with DataTool, click on the red arrow.

17.2.1.2 Choose "comma" and "browse" then select the "groups\lab.me\export data\216" folder and click "OK".

17.2.1.3 Add a backslash (\) and type the data set filename (include ".res" on the end). For example, to export dataset y17wta2, the path appears as "groups\lab_me\exportdata\216\y17wta2.res".

17.2.1.4 Click "OK" to export the data.

17.2.2 If an internal chain-of-custody is required, it is very important that COC forms be filled in correctly and returned to the COC file location. Refer to Attachment 23.5 for an example COC form.

17.3 Laboratory Required Paperwork

17.3.1 Data backup logbook and maintenance logbooks must be filled in completely and correctly. All corrections must be made in indelible ink. **Corrections must be made with a single lineout, which is dated and initialed. Writeovers are NOT acceptable.** Erroneous results must remain legible. A new result is placed near the incorrect result. Blank lines in logbooks must be Z'd out.

18.0 QUALITY ASSURANCE

18.1 All quality control data must be maintained and available for easy reference or inspection. In addition to quality control already discussed, the following requirements apply. Corrective action must be taken for unacceptable quality control results based on instructions given in this procedure, and in TriMatrix SOP GR-10-106.

18.2 Dilute and reanalyze all digestates having concentrations greater than the highest standard on the analytical curve.

18.3 For aqueous samples, include a minimum of one digestion blank (BLK), one high blank spike (BS) and one low blank spike (BS) with each batch of up to twenty samples. For solid samples, include a minimum of one digestion blank (BLK) and one BS with each batch of up to twenty samples. The BLK monitors contamination and carryover while the BS monitors digestion efficiency based on recovery. The BLK and BS must be carried through every step in the digestion and filtration procedure.

18.3.1 A BLK is an aliquot of ASTM Type II water digested as a sample. Any mercury found in the BLK must be at a concentration less than the reporting limit to be acceptable.

18.3.2 A BS is the BLK spiked at a high and low concentration.

18.3.2.1 Calculate BS recovery as follows:

$$\text{Percent Recovery} = \frac{C_{Spike}}{\text{Spike Quantity}} \times 100$$

where:

C_{spike} = The analyzed concentration of the BS after spiking in ug/L or mg/kg

Spike Quantity = The concentration spiked into the BS in ug/L or mg/kg

18.3.2.2 Recovery of the high concentration BS must be within 85 – 115% of the expected value for aqueous samples. Statistical acceptance limits are used for solid samples. Recovery of the low concentration BS must be within 70 – 130% of the expected value. The low concentration BS is for internal use and is not reported.

18.4 Matrix spike and matrix spike duplicates are a sample spiked with a known mercury concentration. Prepare and analyze one matrix spike (MS) and one matrix spike duplicate (MSD) with each batch of up to twenty samples. The matrix spike monitors digestion efficiency in the specific sample matrix. A matrix spike duplicate is a replicate of the matrix spike using the same sample and monitors precision within the sample matrix.

18.4.1 Calculate matrix spike recovery as follows:

$$\text{Percent Recovery} = \frac{C_{Spike} - C_{Orig}}{\text{Spike Quantity}} \times 100$$

where:
C_{spike} = The quantitated MS concentration in ug/L or mg/kg
C_{orig} = The unspiked sample concentration in ug/L or mg/kg
Spike Quantity = The spiked concentration in ug/L or mg/kg

18.4.2 Calculate precision between two spikes using the following equation:

$$\text{Relative Percent Difference} = \left| \frac{C_{MSD} - C_{MS}}{\frac{C_{MSD} + C_{MS}}{2}} \right| \times 100$$

where:
C_{MSD} = The MSD concentration as read from the instrument printout in ug/L or mg/kg
C_{MS} = The MS concentration as read from the instrument printout in ug/L or mg/kg

18.4.3 Matrix spike recovery must be within 70-130% of the expected recovery. However, statistical limits will be used when available but must not exceed 70 – 130%. MSD relative percent difference must be ≤20%.

18.4.4 If MS/MSD criteria fail, reanalyze once. If the second attempt fails, initiate corrective action:

18.4.4.1 Verify the instrument is operating correctly.

18.4.4.2 Verify all other quality control is acceptable.

18.4.4.3 Re-digest the sample and MS/MSD and/or narrate in accordance with TriMatrix SOP GR-10-106.

18.5 Calculate CRL recovery as follows:

$$\text{Percent Recovery} = \frac{C_{Spike}}{\text{Spike Quantity}} \times 100$$

where:

C_{spike} = The analyzed CRL concentration in ug/L
Spike Quantity = The CRL concentration (0.2 ug/L)

18.6 The Method of Standard Additions (MSA)

18.6.1 Use the method of standard additions for all TCLP extracts having 50% or less matrix spike recovery.

18.6.2 Use the method of standard additions on samples from at least one waste stream of an F-waste delisting petition project. If Section 18.6.1 is not met however, apply the method of standard additions to all samples in the delisting.

18.6.3 Standard addition involves adding known mercury concentrations to three sample aliquots. These aliquots are digested and analyzed. The unspiked sample concentration and three spiked aliquots are used to construct a linear regression curve. The curve is extrapolated to find the point where it crosses the x axis. The absolute value of this point is the sample mercury concentration.

18.6.4 Prepare three matrix spikes at 50%, 100%, and 150% of the mercury concentration found in the sample. Final volumes must be the same for each.

18.6.5 Digest and analyze to obtain mercury results for each (in ug/L). Using the MSA regression spreadsheet located on the library drive of the facility network, plot absorbance vs. concentration in ug/L. Construct a linear curve without forcing through the origin. The extrapolated x-intercept point is the sample mercury concentration. An example of an MSA plot is shown in Attachment 23.4. For results to be valid, the following limitations must be taken into consideration:

18.6.5.1 The regression curve must be linear, with a correlation coefficient of ≥0.995 and with a slope less than or equal to 20% of the external calibration curve slope.

18.6.5.2 The chemical form of the mercury added must respond the same way as the mercury in the sample.

18.6.5.3 The interference effect must be constant over the working range of concern.

18.6.5.4 The method of standard additions will not correct for additive interference.

19.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

19.1 Before actual sample analysis, each analyst must demonstrate an ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC) study. A Continuing Demonstration of Capability (CDC) study is also required annually.

19.1.1 Initial Demonstration of Capability (IDC) Study

19.1.1.1 Prepare four second-source blank spikes at a concentration of 2.5 ug/L. Digest, filter and analyze following every step in the procedure.

19.1.1.2 Input the four results to the IDC spreadsheet located on the laboratory intranet library.

19.1.1.3 Average percent recovery must fall within 90 – 110% recovery. Standard deviation of the average must be ≤20% RSD.

19.1.1.4 If either criterion is not met, locate and correct the source of the problem and repeat the study. Repeated failure however, will confirm a general problem with the procedure or techniques used. If this occurs, locate and correct the source of the problem, document changes to the procedure and/or techniques used then repeat the study successfully.

19.1.1.5 Samples may not be analyzed by any analyst until a demonstration of capability study has been successfully completed.

19.1.1.6 Give a copy of successful IDC spreadsheets and raw data to the quality assurance department for training documentation.

19.1.2 Continuing Demonstration of Capability (CDC) Study

19.1.2.1 The demonstration of capability study must be repeated annually.

19.1.2.2 The CDC may be accomplished in one of the following ways:

19.1.2.2.1 By repeating the IDC study

19.1.2.2.2 By using the last four results from an MDL study performed exclusively by the analyst during the course of routine sample analysis. Only the last four results may be used.

19.1.2.2.3 By using four consecutive blank spike results run during the course of routine sample analysis, exclusively by the analyst.

19.1.2.2.4 By successfully and exclusively analyzing a single-blind performance testing sample during the course of routine sample analysis.

19.2 A method detection limit (MDL) study must be completed annually in accordance with TriMatrix SOP GR-10-125 for each digestion procedure.

20.0 POLLUTION PREVENTION

20.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

20.2 Never dispose of laboratory chemicals without first referencing appropriate written instructions of disposal for that particular material.

20.3 Conserve the use of chemicals where applicable.

20.4 Comply with all environmental laws associated with chemicals in the laboratory.

21.0 WASTE MANAGEMENT

21.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals. Material Safety Data Sheets are located on the laboratory intranet library.

21.2 To minimize the environmental impact and costs associated with the disposal of chemicals, order and use only the minimum amount of material required.

21.3 Follow all instructions in TriMatrix SOP GR-15-102 for laboratory waste disposal requirements.

22.0 REFERENCES

22.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Revision 1, September 1994, Method 7470A, "Mercury in Liquid Waste (Manual Cold-Vapor Technique)"

22.2 *Methods for the Determination of Metals in Environmental Samples,* Supplement I, May 1994, Revision 5.4, EMMC Version, "Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry", Method 245.1, Revision 3.0, May, 1994

22.3 *Test Method for Evaluating Solid Waste, Physical/Chemical Methods,* SW-846, 3rd Edition, Final Update III, Revision I, September 1994, Method 7471A, *"Mercury in Solid and Semi Solid Waste* (Manual Cold-Vapor Technique)"

23.0 ATTACHMENTS

23.1 Instrument Maintenance Logbook Example

23.2 Sample Identification and Weighing Sheet Example – Aqueous

23.3 MSA Curve Example

23.4 Internal Chain-of-Custody Example

23.5 Sample Identification and Weighing Sheet Example – Solid

Attachment 23.1
Instrument Maintenance Logbook Example

TriMatrix Laboratories, Inc.

PSA Maintenance Logbook

Date	Analyst	Emission/Reference Readings		Changed Pump Tubes	Changed Lamp	Changed Probe	Replaced Sample Valve	Comments
5.06.03	D.W.							Replaced dryer tube
05/06/03	MSS	196.4	108.8	✓				
05/08/03	DJS/MSS	200.1	110.8	✓				
05/09/03	MSS	185.9	114.1	✓				
05/09/03	MSS	196.1	112.1	✓				
05/13/03	MSS	195.1	114.1	✓				
05/14/03	MSS	190.4	112.2	✓				
05/15/03	MSS	193.1	113.1	✓				
05/16/03	MSS	193.9	111.3	✓				replaced GLS line & Dryer Tube
05/20/03	MSS	200.1	113.2	✓				
05/21/03	MSS	200.0	112.7	✓				
05/22/03	MSS	190.9	107.9	✓				
05/23/03	MSS	199.5	107.1	✓				
05/27/03	MSS	184.1	110.9	✓				replaced GLS line & Dryer Tube
05/28/03	MSS	180.3	107.9	✓				
06/06/03	MSS	197.1	114.0	✓				
06/09/03	MSS	200.1	115.0	✓				
06/11/03	MSS	200.2	114.8	✓				
06/23/03	MSS	200.5	115.1	✓				

file: MaintAvalon.xls page: 3 of 25 revision: 1.0

Attachment 23.2
Sample Identification and Weighing Sheet Example – Aqueous

TriMatrix Laboratories, Inc.

Metals Laboratory Instrument Run Sequence Hg Aqueous

Instrument #: 216
Date:
Analyst:
SnCl #: 8110207

Data File:
Calibration BLK/ICB/CCB: 0.5% HNO3 LOT#1108080
Std/SCV prep date/analyst:

Standards/SCV prepped daily
Autosampler Position:

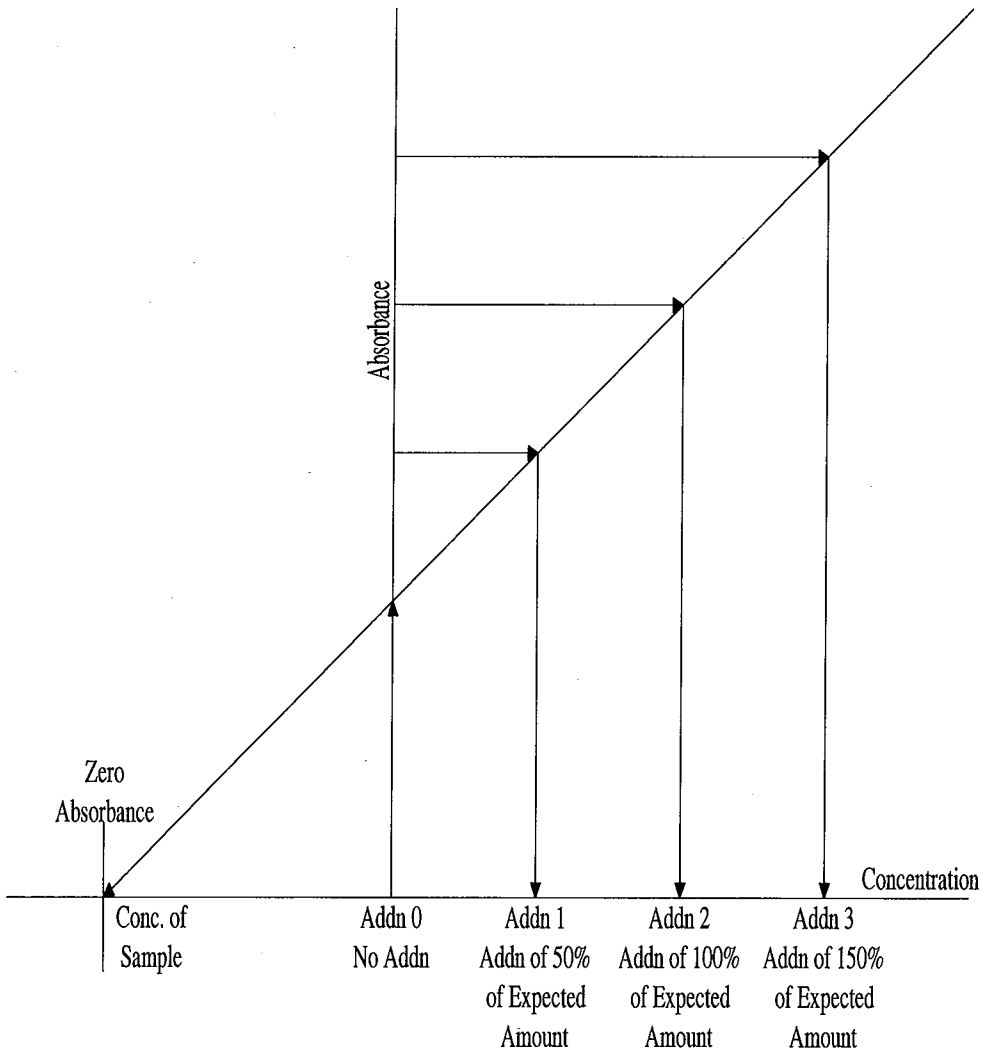
1. BLK/ICB/CCB/8050775
2. STD1/CRL/0.2 ug/L 8050776
3. STD2/0.5 ug/L 8050777
4. STD3/1.0 ug/L 8050778
5. STD4/CCV/2.0 ug/L 8050780
6. STD5/5.0 ug/L 8050781
7. SCV/3.0 ug/L 8100311

Position #	ID	Dilution			Position #	ID	Dilution		
		Initial Volume (mL)	Final Volume (mL)	Dilution Factor			Initial Volume (mL)	Final Volume (mL)	Dilution Factor
11					45				
12					46				
13					47				
14					48				
15					49				
16					50				
17					51				
18					52				
19					53				
20					54				
21					55				
22					56				
23					57				
24					58				
25					59				
26					60				
27					61				
28					62				
29					63				
30					64				
31					65				
32					66				
33					67				
34					68				
35					69				
36					70				
37					71				
38					72				
39					73				
40					74				
41					75				
42					76				
43					77				
44					78				

Hg_AQ.xls revision 1.0

Approved By: 1-15-09 **QA Officer** **Approved By:** 1-19-09 **Area Supervisor**

Attachment 23.3
MSA Curve Example



Attachment 23.4
Internal Chain-of-Custody Example

14-MAY-2003

TRIMATRIX LABORATORIES, INC.
CHAIN OF CUSTODY REPORT FOR AN ENTIRE SUBMITTAL

PAGE #6

CLIENT: MDEQ-RRD
SUBMITTAL: May 7 & 8, 2003 Soils
PROJECT: Former Osceola Refinery West Branch-Sag. Bay Dist.
PROJECT: 35923-7
Parameter: MERCURY, TOTAL
Method: CV/HG/7471/SOL
Ref Cit: USEPA-7471A
Matrix: SOIL

SAMPLE #	REMOVED BY: (SIGNATURE)	DATE & TIME REMOVED	RELINQUISHED BY: DATE & TIME	RECEIVED BY: DATE & TIME	DATE & TIME RETURNED
331322	M.A. Scott			05-5-03 1:30 PM	05-15-03 3:30 PM
331323	MSS				
331324	MSS				
331325	MSS				
331326	MSS				
331327	MSS				
331328	MSS				
331329	MSS				
331330	MSS				
331331	MSS				
331332	MSS				
331333	MSS				
331334	MSS				
331335	MSS				
331336	MSS				
331337	MSS			05-13-03 1:30 PM	05-15-03 3:30 PM

Attachment 23.5
Sample Identification and Weighing Sheet Example – Solid

TriMatrix Laboratories, Inc.

Metals Laboratory Instrument Run Sequence Hg Solids

Instrument #: 216
Date:
Analyst:
SnCl#: 8110207
Data File:
Calibration BLK/ICB/CCB: 0.5% HNO3 LOT#1108080
Std/SCV prep date/analyst:

Standards/SCV prepped daily
Autosampler Position:

1. BLK/ICB/CCB/8050782
2. STD1/CRL/0.2 ug/L 8050784
3. STD2/0.5 ug/L 8050786
4. STD3/1.0 ug/L 8050788
6. STD4/CCV/2.0 ug/L 8050789
6. STD5/5.0 ug/L 8050790
7. SCV/3.0 ug/L 8100310

Position #	ID	Dilution			Position #	ID	Dilution		
		Initial Volume (mL)	Final Volume (mL)	Dilution Factor			Initial Volume (mL)	Final Volume (mL)	Dilution Factor
11					45				
12					46				
13					47				
14					48				
15					49				
16					50				
17					51				
18					52				
19					53				
20					54				
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42					76				
43					77				
44					78				

Hg_solid.xls revision: 1.0

Approved By: 1-15-09 **QA Officer** **Approved By:** 1-19-09 **Area Supervisor**

TriMatrix Laboratories, Inc.

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STANDARD OPERATING PROCEDURE

Synthetic Precipitation Leaching Procedure (SPLP)

SW-846 Method 1312

APPROVALS:

Area Supervisor: Marge A. Scott — Date: 1-13-09
Marge A. Scott

QA Officer: _____ — Date: 1-8-09
Tom C. Boocher

Operations Manager: Jeff Glaser — Date: 1/13/09
Jeff P. Glaser

Procedure Number: GR-01-117
Revision Number: 2.7

Date Initiated: 2/3/96
Effective Date: 1/20/09

Date Revised: 1/7/09
Pages Revised: All

By: Marge A. Scott

Total Number of Pages: 30

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

1.0 SCOPE AND APPLICATION

1.1 This procedure determines the mobility of specific organic and inorganic analytes in liquid, solid and waste matrices.

1.2 An SPLP need not be run if analytes are not detected or are detected but calculated to be below an SPLP regulatory limit. This assessment must be based on a total sample analysis and account for all sample phases. The total analysis can not be reported as the SPLP however.

1.3 If analysis of any liquid fraction of an SPLP leachate indicates a concentration equal to or greater than an SPLP regulatory limit, analysis of the remaining fractions is not required. This assessment applies to multiphasic leachates. Results must be narrated to indicate the results are from only one of multiple leachate phases.

1.4 If the non-volatile leachate concentration of a volatile analyte exceeds an SPLP regulatory limit, the zero-headspace extraction (ZHE) is not performed. However, no non-volatile leachate analysis can demonstrate any volatile analyte concentration to be below an SPLP regulatory limit.

1.5 This procedure applies to SPLP analytes only, except by client request and management approval.

1.6 Filterable oil samples are assumed to have less than 0.5% solids and analysis is performed on the oil filtrate to determine SPLP results. Non-filterable oil and paint samples are assumed to be 100% solids even if appearing to be liquid and are extracted if possible. Otherwise, a total analysis is performed and reported with client approval. No attempt must be made to continue filtering a non-filterable sample by using more than one filter disc or pressure higher than 50 psi. Refer to Attachment 20.9.

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846,* 3rd Edition, Final Update III, December 1996, Method 1312, "Synthetic Precipitation Leaching Procedure", Revision 0, September, 1994

3.0 SUMMARY OF PROCEDURE

3.1 For liquid samples determined to have less than 0.5% dry solid material after filtration through a 0.7 µm glass fiber filter, the filtrate is defined as the leachate.

3.2 For samples determined to have greater than or equal to 0.5% solids, any liquid phase is separated from the solid phase and stored for later use.

3.3 The solid phase particle size is reduced if necessary and extracted with an extraction fluid mass equal to 20 times the dry solid phase mass.

3.4 The extraction fluid employed is a function of the region of the country where the sample site is located, if the sample is a soil. If a sample is waste or wastewater, the extraction fluid used is a pH 4.20 acidic solution.

3.5 A zero-headspace extractor is used when testing for volatile analytes. After the sample tumbles for 18 ±2 hours, the liquid extract is separated from the solid phase by filtration through a 0.7 µm glass fiber filter.

3.6 If compatible (a single phase will form on mixing), any initial sample liquid is added to the SPLP filtrate and the mixture is analyzed as the leachate. If incompatible (two or more phases form on mixing), both and/or all phases must be analyzed separately then mathematically combined to yield a volume-weighted average result.

4.0 PARAMETER OR COMPOUND LIST

4.1 Refer to Attachment 20.1 for the parameters list associated with the SPLP.

4.2 The state of Michigan requires the following additional analytes be evaluated for mobility

4.2.1 Copper, CAS #7440-50-8 at a regulatory limit of 100 mg/L

4.2.2 Zinc, CAS #7440-66-6 at a regulatory limit of 500 mg/L

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal*, latest revision

5.2 TriMatrix SOP GR-01-119, Toxicity Characteristic Leaching Procedure (TCLP), latest revision

5.3 TriMatrix SOP GR-09-104, *Waste Dilution for Semi-Volatile BNA Compounds*, latest revision

5.4 TriMatrix SOP GR-04-103, *Semi-volatiles Gas Chromatography Mass Spectrometry(GC/MS) Base Neutral Acids(BNA)*, latest revision

5.5 TriMatrix SOP GR-03-126, *Chlorinated Herbicides by Capillary Column Gas chromatography*, latest revision

5.6 TriMatrix SOP GR-09-113, *Extraction of Chlorinated Herbicides from Water and Wastewater*, latest revision

5.7 TriMatrix SOP GR-09-101, *Extraction Base Neutrals Acids(BNA) from Water*, latest revision

5.8 TriMatrix SOP GR-09-107, *Extraction Organochlorine Pesticides and PCBs from Water*, latest revision

5.9 TriMatrix SOP GR-03-120, *Gas Chromatography(GC) Organochlorine Pesticides*, latest revision

5.10 TriMatrix SOP GR-01-147, *Acid Digestion of Total Metals in Aqueous Samples by Block Digestion for ICP*, latest revision

5.11 TriMatrix SOP GR-07-100, *Potentiometric pH*, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Interferences and corrective procedures are discussed in each TriMatrix procedure associated with leachate analysis.

7.0 SAFETY PRECAUTIONS

7.1 Be certain non-volatiles tumbler vessels are well vented before tumbling. Each vessel must be checked periodically for internal pressure and leakage. Vent tumbler vessels cautiously to prevent injury from explosive sample loss.

7.2 If a tumbler vessel breaks, leaks or otherwise causes a significant spill, notify the area supervisor and safety officer. Refer to the Laboratory Safety Manual for appropriate clean-up and dispose of any spill material appropriately.

7.3 Analysts must comply with all instructions for health and safety as outlined in the TriMatrix Laboratory Safety Manual and Chemical Hygiene Plan.

7.4 Approved safety glasses and disposable gloves must be worn when performing any aspect of this procedure and/or when working in the laboratory. Laboratory coats are also required.

7.5 Keep laboratory coats and/or loose clothing away from rotating tumbler apparatus.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Collect samples using a sampling plan appropriate to data objectives.

8.2 There are requirements on the minimum sample size collected, depending on the physical characteristics of the sample and target analytes. An aliquot is required for preliminary percent solids and particle size determinations. An aliquot is required for the non-volatile extraction. Quality control requires additional aliquots. It is advisable to collect additional sample volume/mass in case something occurs during the SPLP to invalidate results.

8.3 Preservatives must not be added to samples before extraction.

8.4 Samples may be refrigerated unless refrigeration results in an irreversible physical change. If precipitation occurs, the entire sample (including precipitate) must be extracted.

8.5 Leachates must be preserved and analyzed as soon as possible following extraction. Preservation must be as instructed in the appropriate analytical procedure.

8.6 Sample/leachate holding times are as follows:

Analysis	From Collection to Extraction	From Extraction to analysis pre-treatment	From pre-Treatment to Analysis	Total Elapsed Time
Volatiles	14	not applicable	14	28
semi-Volatiles	14	7	40	61
Mercury	28	not applicable	28	56
Metals except Mercury	180	not applicable	180	360

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Extraction tumblers, capable of rotating end-over-end at 30 ±2 rpm are as follows:

9.1.1 Non-volatile rotary tumblers, privately fabricated for use at TriMatrix Laboratories

9.1.2 Zero-headspace extraction tumblers, purchased from Millipore Corporation

9.2 Zero-Headspace Extraction Vessels

9.2.1 Zero-headspace extraction (ZHE) vessels must be used when a sample is evaluated for volatile analytes mobility. The ZHE vessel is designed to perform liquid phase/solid phase separation, the introduction of extraction fluid, the SPLP and leachate filtration without opening. The ZHE has an internal volume of 500 to 600 mL and is equipped to accommodate a 90-110 mm, 0.7 µm glass fiber filter.

9.2.2 The ZHE piston must move with no higher than 15 psi. If not, the fluoroelastomer O-rings must be replaced. If replacing O-rings does not decrease the pressure required to move the piston, the ZHE must be repaired by the manufacturer before using or be replaced.

9.2.3 A ZHE must be tested for leaks after every extraction by pressurizing to 50 psi and letting sit unattended for one hour. If pressure is lost, check all fittings and inspect or replace the O-rings. Repeat the leak test after repairs are made. If leakage problems can not be solved, the ZHE must be repaired by the manufacturer before using or replaced.

9.3 Extraction Vessels for non-volatile analytes

9.3.1 Vessels with sufficient volume to hold sample solids and extraction fluid must be used. Headspace is not an issue. However, any vessel used must be inert to the sample being extracted.

9.3.2 Borosilicate glass vessels with a PTFE-lined lid are used when evaluating metals and semi-volatiles mobility from the same extraction.

9.3.3 High density polyethylene (HDPE) vessels are used when evaluating only metals.

9.4 Filtration Equipment

9.4.1 Filtration equipment must be inert to the sample being extracted. If using PTFE-coated stainless steel, the coating must unbroken.

9.4.2 When a sample is evaluated for volatiles mobility, the ZHE vessel is used for filtration. A ZHE supports and holds a 0.7 µm glass fiber filter. The vessel is designed to withstand up to 50 psi without rupturing the filter.

Note: If a filter ruptures, a gas-tight syringe and syringe filter must be used to remove the filtrate for transfer to a Tedlar® bag.

9.4.3 A positive-pressure filter holder is used when a sample is evaluated for metals and semi-volatiles mobility. The holder has an internal capacity of 1.5 L, accommodates a 142 mm diameter 0.7 µm glass fiber filter and is capable of exerting 50 psi or greater. Vacuum filtration is not used.

9.4.4 Assemble and operate pressure filters and ZHE vessels in accordance with the manufacturer's instructions.

9.5 Borosilicate glass fiber filters not containing binder material, with an effective pore size of 0.7 µm are used for all filtrations. Pre-filters must not be used. Borosilicate glass fiber filters are fragile and must be handled with care.

9.5.1 When evaluating metals mobility, the filter must be acid-washed before using by washing with 1N nitric acid.

9.5.2 Follow with three consecutive rinses of laboratory reagent water. Use approximately 1 L per rinse.

9.6 The pH meter used must be accurate to 0.05 units at 25° C and must be used in accordance with TriMatrix SOP GR-07-100.

9.7 A polyvinyl fluoride Tedlar® bag or 500 mL glass gas-tight syringe must be used to collect any initial liquid phase and the ZHE leachate as follows:

9.7.1 If a sample contains an aqueous liquid phase and less than 1% filterable non-aqueous liquid, a Tedlar® bag or 500 mL glass gas-tight syringe is used to collect and combine the initial liquid sample phase and extracted solids filtrate.

9.7.2 If a sample contains greater than 1% non-aqueous filterable liquid (such as oil), a Tedlar® bag is used to collect the initial filtrate (oil) and a separate Tedlar® bag is used to collect the extracted solids filtrate.

9.7.3 If a sample contains no initial liquid phase (is 100% extractable solid) or has no significant solid phase (is 100% liquid), a Tedlar® bag is used to collect the sample filtrate (100% filterable liquid) or leachate (100% non-filterable solid).

9.8 A ZHE extraction fluid transfer device is used to transfer extraction fluid into the ZHE without changing the nature of the extraction fluid.

9.9 Balance, analytical, accurate to within 0.01 g

9.10 Beaker and/or Erlenmeyer flasks, glass or Pyrex, 500 mL

9.11 Watchglasses, glass, appropriate diameters to cover beakers or Erlenmeyer flasks

9.12 Sieve, 9.5 mm (0.375 inch)

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 Rotary Tumblers

10.1.1 Wash weekly with warm soapy water and rinse thoroughly with warm water

10.1.2 Oil motors weekly

10.1.3 Monitor the tumbler room temperature with each use

10.1.4 The plastic tumbler vessel packing material that holds a vessel inside the tumbler must be changed with each sample rotated.

10.1.5 Monitor and record revolutions per minute (rpm) for each rotary tumbler. Tumbler velocity must be 30 ±2 rpm. If velocity exceeds 30 ±2 rpm perform maintenance and repair of the motor and/or bearings.

10.2 pH meters

10.2.1 Maintain and calibrate in accordance with TriMatrix SOP GR-07-100.

10.2.2 Rinse probes with laboratory reagent water after each immersion into a solution.

10.3 Filtration Devices

10.3.1 Change gaskets and O-rings as needed.

10.3.2 Frequently examine the PTFE coating on interior ZHE surfaces. Scored or abraded surfaces inhibit effective decontamination. If scored or abraded, return to the manufacturer for recoating.

10.2 ZHE Vessels

10.2.1 Replace fluoroelastomer O-rings before each extraction.

10.2.2 Replace worn gaskets as needed.

10.2.3 Maintain pressure gauges and replace as needed.

10.2.4 Check for leaks between each use.

11.0 CHEMICALS AND REAGENTS

11.1 Trace metal grade acids must be used. All other reagents must conform to specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications exist.

11.2 Laboratory reagent water

11.2.1 For nonvolatile extractions, ASTM Type II water (MilliQ system) is used.

11.2.2 For ZHE extractions, ASTM Type II water is passed through two carbon black filters and one small carbon filter, and is purged with nitrogen gas for a minimum of 30 minutes before using.

11.2.3 Both reagent waters must be checked for contamination and interference by extraction blanks.

11.3 Sulfuric acid (H_2SO_4)/nitric acid (HNO_3), 60:40 (wt/wt), prepared by cautiously mixing 60 g of concentrated H_2SO_4 with 40 g of concentrated HNO_3. Store in a glass container.

11.4 Extraction fluids

11.4.1 Extraction fluid #1 is prepared by adding 60:40 H_2SO_4/HNO_3 (wt/wt) to the appropriate laboratory reagent water until the apparent pH is 4.20 ±0.05. Extraction fluid #1 is used to determine mobility in soil from collection sites east of the Mississippi River. It is also used to determine waste and wastewater solids mobility.

Note: Solutions are unbuffered and accurate pH may not be determinable. The apparent pH is sufficient.

11.4.2 Extraction fluid #2 is prepared by adding 60:40 H_2SO_4/HNO_3 (wt/wt) to the appropriate laboratory reagent water until the pH is 5.00 ±0.05. Extraction fluid #2 is used to determine mobility in soil from collection sites west of the Mississippi River.

11.4.3 Extraction fluid #3 is laboratory reagent water, and is used to determine cyanide and volatiles mobility.

Note: These extraction fluids must be monitored for impurities and pH with extraction blanks. If impurities are found or the pH is not within the above specifications, discard and prepare fresh extraction fluid. Samples associated with contaminated extraction blanks must be re-extracted and/or narrated.

11.5 Nitrogen gas, industrial grade or better

12.0 STANDARDS PREPARATION

12.1 There is no standards preparation directly associated with this procedure.

13.0 ANALYTICAL PROCEDURE

13.1 Perform preliminary evaluations on a minimum 100 g sample aliquot. This aliquot does not undergo subsequent SPLP unless otherwise specified.

13.2 Preliminary evaluations include:

13.2.1 Percent extractable solids determination by filtration.

13.2.2 Percent dry solids determination by filtration and drying.

13.2.2 Particle size determination.

13.2.3 Determination of which extraction fluid is used. Use the Extraction Worksheet (Attachments 20.5, 20.6, 20.7 and 20.8) as a step-by-step guide and as a logbook for recording sample evaluations.

13.3 Percent extractable solids (Section 2.0 on the Extraction Worksheet) are defined as the sample fraction (as a percentage of the total sample) from which no liquid may be forced out by applied pressure, as described below:

13.3.1 If a sample will obviously yield no liquid when subjected to pressure filtration (is 100% extractable solids) proceed to Section 13.4.

13.3.2 If a sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent extractable solids is required. This involves the pressure filter holder described in Section 9.4 and is outlined below.

13.3.2.1 Pre-weigh the filter disc and container receiving the filtrate.

13.3.2.2 Assemble the filter holder and filter by placing the filter on the support screen and securing.

13.3.2.3 Weigh out a sample aliquot (100 g minimum) and record the mass.

13.3.2.4 Let slurries stand to permit solid particles to settle out before filtering. Samples that settle slowly may be centrifuged. However, centrifugation must be used only as a filtration aid. If used, decant any liquid into the filter before adding the solid phase. Filter the entire aliquot by making a quantitative transfer into the filter holder but do not rinse.

13.3.2.5 Spread non-filterable solids evenly over the filter surface. Filtration must be at room temperature to prevent viscosity changes from affecting the determination.

Note: If greater than 1% of the original mass obviously adheres to the transfer container, determine the mass of this residue and subtract it from the original aliquot mass recorded. The actual mass transferred must be used.

13.3.2.6 Gradually apply gentle pressure from 1-10 psi, until liquid moves through the filter. If no additional liquid passes through the filter after being at 1-10 psi for two minutes, slowly increase the pressure in 10 psi increments at 2-minute intervals to a maximum of 50 psi. When the liquid flow ceases at 50 psi or only gas is passing through the filter, wait two minutes then stop the filtration.

Note: Instantaneous application of pressure degrades the glass fiber filter and causes plugging. Pressure increases must be very gradual. Especially below 10psi.

13.3.2.7 Any non-filterable sample remaining on the filter is defined as the extractable portion of the sample except as specified in Section 1.6.

13.3.2.8 Determine liquid phase mass by subtracting the filtrate container mass from the total filtrate/container mass. Determine the solid phase mass by subtracting the liquid phase mass from the sample aliquot used. Record the liquid and solid phase masses and calculate percent extractable solids as follows:

Percent Solids = $(M_s / M_w)*100$

Where:
M_s = Solid phase, in grams
M_w = Sample aliquot used, in grams

13.4 Calculate percent dry solids on the non-filterable sample fraction as follows:

13.4.1 To dry the solid phase from a percent extractable solids determination, remove the solid phase and filter from the filtration apparatus.

13.4.2 Dry the filter and solid phase at 100 ±20° C until two successive weighings yield the same value to within 1%. Record the final dry mass.

Note: Caution must be taken to ensure a solid phase will not flash and/or ignite when heated. Although the drying oven is vented, do not oven-dry organic solids such as oils, unknown chemicals and/or other low-flashpoint materials.

13.4.3 Calculate percent dry solids as follows:

$S_d = (M_{w+f} - M_f)*100/M_w$

Where:
M_{w+f} = Dry sample and filter mass, in g
M_f = Filter mass, in g
M_w = Total sample mass evaluated, in g
S_d = Dry solids, in %

13.5 When percent dry solids are less than 0.5%, proceed to Section 13.9 if a non-volatiles extraction is required. Proceed to Section 13.10 if a volatiles extraction is required. If dry solids are equal to or greater than 0.5%, use a fresh sample aliquot to determine whether particle size reduction is necessary and to determine which extraction fluid is required.

13.6 Solid phase particle size reduction

13.6.1 Particle size reduction is required before extraction unless a solid has a surface area equal to or greater than 3.1 cm^2/g, or is smaller than 1 cm in its narrowest dimension. It must be capable of passing through a 9.5 mm standard sieve.

13.6.2 If a solid phase will not pass through the sieve, reduce particle size by crushing, cutting, or grinding until it does. Record all steps taken to reduce particle size on the Extraction Worksheet in Sections 2.3, 3.2 and 4.4.

Note: Surface area criteria are meant for filamentous paper, cloth, and similar materials. Actual surface area measurement after particle size reduction is not required.

13.7 If a solid phase is greater than or equal to 0.5% and will be extracted for non-volatiles, determine the appropriate extraction fluid as follows (Section 3.0 on the Extraction Worksheet):

13.7.1 Use extraction fluid #1 for soils collected from a site east of the Mississippi River.

13.7.2 Use extraction fluid #2 for soils collected from a site west of the Mississippi River.

13.7.3 Use extraction fluid #1 for waste and wastewater samples.

13.7.4 Use extraction fluid #3 for cyanide mobility in all sample matrices.

13.7.5 Use extraction fluid #3 for all volatile ZHE evaluations.

13.8 If the sample aliquot used for preliminary evaluation is 100% solid, it can be used for the non-volatiles extraction (assuming at least 100 g remain). The aliquot used for percent solids determination is also appropriate for non-volatiles extraction if enough solid was obtained to support all analyses required and the aliquot was not oven-dried. If an adequate quantity remains, proceed to Section 13.9. If a sample is not a 100% solid and a dry solids determination was done, another aliquot must be taken for extraction. A new aliquot must always be taken for ZHE.

13.9 Extraction for non-volatiles

13.9.1 For a non-volatiles extraction, use at least 100 g of wet sample (Section 4.0 to 7.0 on the Extraction Worksheet). A larger aliquot may be needed depending on percent solids, on whether any initial liquid phase is miscible with the solid phase extract and on the analytes targeted. Enough leachate must be obtained to support all analyses requested. If the leachate volume generated from a single extraction is insufficient to support all analyses, extract another sample aliquot and combine the leachates before analysis.

13.9.2 If a sample yields no liquid when subjected to pressure filtration (is 100% extractable solids and does not need particle reduction), weigh out at least 100 g and proceed to Section 13.9.4.

13.9.3 If a sample is liquid or multiphasic, pressure filtration is required as follows:

13.9.3.1 Pre-weigh the container receiving filtrate.

13.9.3.2 Assemble the filter holder and filter. Place the filter on the support screen and secure. Acid-wash the filter if evaluating metals mobility.

Note: Acid-washed filters may be used for any non-volatile extraction, even when metals are not targeted.

13.9.3.3 Weigh out at least 100 g of sample and record the mass. If a sample contains <0.5% dry solids, the liquid filtrate is defined as the leachate. Enough sample must be filtered so the volume can support all required analyses. For samples containing ≥0.5% dry solids, use the percent solids value obtained earlier to determine the minimum sample mass over 100 g needed to support all required analyses.

13.9.3.4 Let sedimentary samples settle before filtering. Samples that settle slowly may be centrifuged. However, centrifugation must be used only as a filtration aid. If used, decant any liquid into the filter before adding the solid phase. Filter the entire aliquot by making a quantitative transfer into the filter holder, without rinsing.

13.9.3.5 Spread non-filterable solids evenly over the filter surface. Filtration must be at room temperature to prevent viscosity changes from affecting results.

Note: If greater than 1% of the original mass obviously adheres to the transfer container, determine the adhering residue mass and subtract it from the original aliquot mass recorded. This determines the actual mass transferred to the filter.

13.9.3.6 Gradually apply gentle pressure up to 10 psi, until liquid moves through the filter. If no additional liquid passes through the filter after being at 10 psi for two minutes, slowly increase the pressure in 10 psi increments at 2-minute intervals to a maximum of 50 psi. When the liquid flow ceases at 50 psi or only gas is passing through the filter, wait two minutes then stop the filtration.

Note: Instantaneous application of pressure degrades the glass fiber filter and causes plugging. Pressure increases must be gradual. Especially pressure applied below 10psi.

13.9.3.7 Sample remaining on the filter is defined as the solid phase which must be extracted except as specified in Section 1.6. Any filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase is analyzed as the leachate if dry solids are less then 0.5%. If not, the liquid phase must be stored at 4 ±2° C until the solid phase is extracted.

13.9.3.8 If a sample contains <0.5% dry solids, proceed to Section 13.9.8 with the sample filtrate. If a sample passes the 9.5 mm sieve as received, transfer the solid phase and filter into an extraction bottle then proceed to Section 13.9.4.

13.9.3.9 Prepare solid phases for extraction by crushing, cutting or grinding to a surface area or particle size that will pass through the 9.5 mm sieve. When surface area or particle size has been reduced, transfer into an extraction bottle. Include the filter used to separate the initial liquid from the solid phase.

13.9.4 Determine the volume of extraction fluid needed as follows:

$M_{ext\ fluid} = (20/100)*S_d*M_w$

Where:

$M_{ext\ fluid}$ = Extraction fluid needed, in g
M_w = Total sample aliquot used, in g
S_d = Dry solids, in %

13.9.5 Check the extraction fluid pH and record in the Extraction Fluid Logbook (Attachments 20.2, 20.3 and 20.4). Slowly add extraction fluid to the extraction bottle. Close the lid tightly using PTFE tape to ensure a tight seal. Secure in the tumbler and rotate at 30 ±2 rpm for 18 ±2 hours. The extraction room temperature must be maintained at 23 ±2° C during the extraction.

Note: While tumbling, pressure may build within extraction vessels containing lime or calcium carbonate samples. To prevent excess pressure, extraction vessels must be opened after extracting for 15 minutes, 30 minutes and 1 hour for all samples.

13.9.6 Following extraction, filter the extract fluid through a new 0.7 µm glass fiber filter as outlined previously. The filter may be changed if necessary, to speed up filtration. Filters must be acid-washed if evaluating metals mobility.

13.9.7 Complete the extraction as follows:

13.9.7.1 If a sample contains no initial liquid phase, the extraction bottle filtrate is the complete leachate.

13.9.7.2 If a sample contains multiple phases, combine the entire extraction bottle filtrate with the initial liquid phase filtered from the sample aliquot used. The combined filtrate is the leachate.

13.9.7.3 If the initial liquid phase from a sample does not appear miscible with extraction bottle filtrate, do not combine. Each must be analyzed separately and the combined leachate result must be obtained mathematically.

13.9.8 Following collection of the complete leachate, check and record the pH then immediately aliquot the leachate for preservation and analysis.

13.9.8.1 Metals aliquots must be acidified with nitric acid to pH <2. If precipitation occurs when nitric acid is added to a small volume, do not preserve and digest as soon as possible.

13.9.8.2 All aliquots must be stored at 4 ±2° C unless prepared for analysis immediately.

13.9.8.3 After filtering, prepare the leachate for analysis immediately. Store with minimal headspace at 4 ±2° C until analysis. Analyze leachates according to the appropriate analytical procedure. If a leachate contains multiple phases, determine the volume of each phase to 0.5% and analyze both then combine results mathematically as follows:

Final Analyte

$$Concentration = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

Where:

V_1 = Volume of the first phase, in L
C_1 = Analyte concentration in the first phase, in mg/L
V_2 = Volume of the second phase, in L
C_2 = Analyte concentration in the second phase, in mg/L

13.9.9 Report leachate concentrations in mg/L.

13.10 Volatiles Extraction

13.10.1 When volatiles analysis is required, ZHE must be performed and the ZHE worksheet (Attachments 20.7 and 20.8) must be completed. Leachates obtained from a ZHE must not be analyzed for metals or semi-volatile organic compounds.

13.10.2 A ZHE has approximately 500 mL internal capacity. No more than 25 g of solid phase can be extracted. Only non-filterable sample is extracted.

13.10.3 Introduce sample into the ZHE extractor once and do not open until the leachate has been collected. Repeated filling to obtain 25 g of solid from a low-solids sample is not permitted.

13.10.4 Do not expose samples, initial liquid phases or extracts to the air for any more time than absolutely necessary. Handle these materials while cold (approximately 4° C) to minimize volatiles loss.

13.10.5 Pre-weigh an evacuated Tedlar® bag and set it aside. Express the extraction filtrate directly into the bag unless the ZHE filter has broken.

13.10.6 Moisten the piston O-rings with extraction fluid and place the ZHE piston within the body of the ZHE. Adjust the piston within the ZHE body to a height that minimizes the distance the piston moves once the ZHE is charged with sample. Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body. Secure the glass fiber filter between the support screens and set aside. Set the liquid inlet/outlet flange (top flange) aside.

13.10.6.1 If a sample is 100% solids, weigh out no more than 25 g and record the mass.

13.10.6.2 If a waste contains <0.5% dry solids, the liquid filtrate is the TCLP extract. Weigh out up to 500 g for charging and record the mass.

13.10.6.3 If a waste contains ≥ 0.5% dry solids, weigh out a calculated sample charging mass up to 500 g and record. Calculate the charging mass to weigh out as follows:

Sample charging mass (g) = (25*100)/percent dry solids

13.10.7 If solid phase particle size reduction is required, crush, cut, or grind to a surface area or particle size as previously described.

13.10.7.1 The solid phase and reduction equipment must be cooled to approximately 4° C before performing the reduction.

13.10.7.2 The technique used must not generate heat.

13.10.7.3 Avoid exposure to the air during particle reduction to the highest extent possible.

13.10.7.4 Use a graduated ruler instead of sieving to estimate particle size.

13.10.8 Do not let slurries stand for solid phase settling. Do not centrifuge before charging the ZHE.

13.10.9 Rapidly and quantitatively transfer the entire sample (all phases) into the ZHE without rinsing. Secure the filter and support screens onto the top flange and secure the top flange to the ZHE body. Tighten all ZHE fittings and place in a vertical position with the gas inlet/outlet flange down. If greater than 1% of the original sample mass obviously adheres to the transfer container, determine the residue's mass and subtract it from the sample charging mass.

13.10.10 Attach a gas line to the gas inlet/outlet valve on the bottom flange then with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-15 psi to force all headspace out of the ZHE. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If 4° C inhibits filtration, let the sample warm to room temperature in the ZHE before filtering.

13.10.11 Attach the evacuated pre-weighed Tedlar® bag to the liquid inlet/outlet valve then open the valve. Begin applying gentle pressure of 1-10 psi to force any liquid phase into the bag. If no additional liquid passes through the filter after being at 1-10 psi for two minutes, slowly increase the pressure in 10 psi increments at 2-minute intervals to a maximum of 50 psi. When the liquid flow ceases at 50 psi, wait two minutes then stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, then disconnect and weigh the Tedlar® bag.

Note: Instantaneous application of pressure degrades glass fiber filters and causes premature plugging. Always increase the pressure gradually.

13.10.12 Non-filterable material remaining in a ZHE after sample filtration is the solid phase except as specified in Section 1.6. The filtrate is the liquid phase. Place Tedlar® bags containing liquid phase in the walk-in cooler until the solid phase has been extracted and the leachate can be combined with the liquid sample phase. All Tedlar® bags containing liquid phase or leachate must be labeled appropriately.

13.10.13 Add extraction fluid to the ZHE as follows:

13.10.13.1 With the ZHE in the vertical position, attach a line from the fluid reservoir to the liquid inlet/outlet valve. The line used must be pre-flushed with fluid to eliminate air pockets. Release pressure on the ZHE piston from the gas inlet/outlet valve, open the liquid inlet/outlet valve and pump the calculated volume of extraction fluid into the ZHE.

13.10.13.2 After adding, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure all valves are closed. Manually rotate the ZHE end-over-end 2 or 3 times. Reposition in the vertical position with the liquid inlet/outlet valve on top. Pressurize enough to move the piston (about 5-15 psi) then slowly open the liquid inlet/outlet valve to bleed any headspace from introducing extraction fluid. The bleeding must be done quickly and stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE to 5-10 psi and check all fittings to ensure each is closed.

13.10.13.3 Place in a ZHE rotary tumbler and rotate at 30 ±2 rpm for 18 ±2 hours. Monitor and record the extraction room temperature which must be maintained at 23 ±2° C during the extraction.

13.10.14 Following extraction, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas.

13.10.14.1 If no gas release is observed, the extractor has leaked. Check for leaks as specified in Section 9.2.3. If the ZHE has leaked, repair or replace the ZHE unit and repeat the extraction with a new sample aliquot.

13.10.14.2 If the extractor has not leaked, the leachate must be filtered. If the liquid sample phase is compatible, filter directly into the same Tedlar® bag. If the liquid sample phase is not compatible and/or will form a two-phase leachate, filter into another Tedlar® bag. If the combined extracts exceed the volume capacity of one bag use a separate Tedlar® bag.

13.10.14.3 Filter through the glass fiber filter already in the ZHE by increasing pressure gradually, as discussed previously. All extraction fluid must be filtered and collected if a Tedlar® bag is used, if a leachate is multiphasic or if the sample extracted contains an initial liquid phase.

Note: An in-line glass fiber filter may be used if it is suspected the glass fiber filter in the ZHE has ruptured.

13.10.15 If a sample contains no initial liquid phase, the ZHE filtrate is the leachate. If a sample contains an initial liquid phase, the combined ZHE and initial liquid phase filtrates are the leachate.

13.10.16 After filtering, prepare the leachate for analysis immediately. Store with minimal headspace at 4 ±2° C until analysis. Analyze leachates according to the appropriate analytical procedure. If a leachate contains multiple phases, determine the volume of each phase to 0.5% and analyze both then combine results mathematically as follows:

Final Analyte

$$Concentration = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

Where:

V_1 = Volume of the first phase, in L
C_1 = Analyte concentration in the first phase, in mg/L
V_2 = Volume of the second phase, in L
C_2 = Analyte concentration in the second phase, in mg/L

13.10.17 Report leachate concentrations in mg/L.

14.0 DATA REPORTING AND DELIVERABLES

14.1 Data must be collected in accordance with the TriMatrix Quality Assurance Manual.

14.2 Data required for entry into the laboratory LIMS system (Element™) is to be collected on the extractions worksheet.

14.3 All data recorded from evaluating samples must be organized and archived appropriately.

15.6 The SPLP logbook is to be filled in completely for both volatiles and semi-volatiles during the initial set-up/percent solids, extraction fluid and pH determinations. Final leachate filtration steps such as pH measurement, time completed, pH meter number must also be recorded.

15.7 The TriMatrix laboratory report does not include an assessment of waste stream characterization except by listing SPLP applicable regulatory limits with sample results. However, the client must be notified as soon as possible of unusual or abnormal results above any known regulatory limit.

15.0 QUALITY ASSURANCE

15.1 Extract a minimum of one non-volatiles extraction blank for each extraction fluid used for samples, for every 20 extractions conducted, for each extraction vessel lot used.

15.2 Extract a minimum of one ZHE blank for each ZHE unit, after every 20 extractions conducted. ZHE extraction vessels are labeled "A" through "N".

15.3 A post-SPLP matrix spike shall be performed for each sample type extracted in the 20-sample extraction batch. A minimum of one post-SPLP matrix spike must be analyzed for each extraction batch.

15.3.1 Leachate aliquots of the same volume used for sample analysis must be matrix-spiked before preservation. Do not spike prior to the SPLP extraction.

15.3.2 Matrix spike concentrations are designated in the appropriate analytical procedure.

15.3.3 If matrix spike recovery is less than 50% for a metallic analyte, the method of standard additions is required for quantitation of all samples of the same matrix type in the batch.

15.4 All quality control in the analytical procedure must be followed and within acceptable control limits for leachate analysis and reporting.

15.5 If sample and/or leachate holding times are exceeded, the values obtained must be narrated as minimal concentrations.

15.6 If a tumbler vessel breaks during extraction, the sample must be re-extracted with another sample aliquot.

15.7 If the extraction is shut down for longer than any ½-hour period during the 18-hour extraction, samples in the tumbler must be re-extracted with another sample aliquot.

15.8 Minimum leachate volumes are required for analysis and quality control as follows:

15.8.1 Base/neutral/acid compounds, pesticides and herbicides analysis groups require at least 1.5 L of leachate each (preferably 2 L) when quality control is performed. Otherwise, at least 25 g of dry sample solids must be extracted for each group evaluated with at least 100 g of wet sample evaluated. Calculate minimum sample aliquots to use based on percent dry solids.

15.8.2 The metals analysis group requires at least 200 mL of leachate for all samples. At least 10 g of dry sample solids must be extracted with at least 100 g of wet sample evaluated. Calculate minimum sample aliquots to use based on percent dry solids.

15.8.3 The volatiles analysis group requires at least 120 mL of leachate. At least 6 g of dry sample solids must be extracted with at least 25 g of wet sample evaluated. Calculate minimum sample aliquots to use based on percent dry solids.

Note: Extractions for non-volatile organic groups must be tumbled in 4 L borosilicate glass vessels with PTFE-lined lids.

15.9 Extraction fluids #1 and #2 are made in 50 L volumes and given a batch number. A full-analyte extraction blank and matrix spike must be evaluated for each batch made. If interference and/or contamination are found at concentrations higher than any minimum reporting limit, the batch is not to be used for sample evaluation. All extraction fluid evaluation data is to be maintained in accordance with the TriMatrix Quality Assurance Manual.

16.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

16.1 There is no quantitative demonstration of capability directly associated with this procedure.

16.2 Analyst training is to be conducted in accordance with the TriMatrix Quality Assurance Manual.

17.0 POLLUTION PREVENTION

17.1 Maintain an inventory of all chemicals used in the laboratory to monitor their use.

17.2 Never dispose of any laboratory chemical without first referencing appropriate written instructions of disposal for that particular material.

17.3 Conserve the use of chemicals where applicable

17.4 Comply with all environmental laws associated with chemicals in the laboratory.

18.0 WASTE MANAGEMENT

18.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals.

18.2 To minimize the environmental impact and costs associated with chemical disposal, order and use only the minimum amount of material required.

18.3 Follow all instructions in TriMatrix Laboratory SOP GR-15-102 for laboratory waste disposal.

18.4 If a sample contains unusually high contaminant concentrations, arrangements may be made to return unused portions of the sample to the client for disposal purposes.

19.0 REFERENCES

19.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846,* 3rd Edition, Final Update III, December 1996, Method 1312, "Synthetic Precipitation Leaching Procedure", Revision 0, September, 1994

19.0 ATTACHMENTS

20.1 Toxicity Characteristic Regulated Analytes List

20.2 Extraction Fluid #1 Logbook Example

20.3 Extraction Fluid #2 Logbook Example

20.4 Extraction Fluid #3 Logbook Example

20.5 Extraction Worksheet Example, Page 1

20.6 Extraction Worksheet Example, Page 2

20.7 Extraction Worksheet Example for ZHE, Page 1

20.8 Extraction Worksheet Example for ZHE, Page 2

20.9 United States Environmental Protection Agency Memorandum 35, page 10

Attachment 20.1
Toxicity Characteristic Regulated Analytes List

Maximum Concentration of Contaminants for the Toxicity Characteristic

EPA HW No. \1\	Contaminant	CAS No.\2\	Regulatory Level (mg/L)
D004	Arsenic.....	7440-38-2	5.0
D005	Barium.....	7440-39-3	100.0
D018	Benzene.....	71-43-2	0.5
D006	Cadmium.....	7440-43-9	1.0
D019	Carbon tetrachloride.....	56-23-5	0.5
D020	Chlordane.....	57-74-9	0.03
D021	Chlorobenzene.....	108-90-7	100.0
D022	Chloroform.....	67-66-3	6.0
D007	Chromium.....	7440-47-3	5.0
D023	o-Cresol.....	95-48-7	\4\ 200.0
D024	m-Cresol.....	108-39-4	\4\ 200.0
D025	p-Cresol.....	106-44-5	\4\ 200.0
D026	Cresol.....	.....	\4\ 200.0
D016	2,4-D.....	94-75-7	10.0
D027	1,4-Dichlorobenzene.....	106-46-7	7.5
D028	1,2-Dichloroethane.....	107-06-2	0.5
D029	1,1-Dichloroethylene.....	75-35-4	0.7
D030	2,4-Dinitrotoluene.....	121-14-2	\3\ 0.13
D012	Endrin.....	72-20-8	0.02
D031	Heptachlor (and its epoxide).	76-44-8	0.008
D032	Hexachlorobenzene.....	118-74-1	\3\ 0.13
D033	Hexachlorobutadiene.....	87-68-3	0.5
D034	Hexachloroethane.....	67-72-1	3.0
D008	Lead.....	7439-92-1	5.0
D013	Lindane.....	58-89-9	0.4
D009	Mercury.....	7439-97-6	0.2
D014	Methoxychlor.....	72-43-5	10.0
D035	Methyl ethyl ketone.....	78-93-3	200.0
D036	Nitrobenzene.....	98-95-3	2.0
D037	Pentrachlorophenol.....	87-86-5	100.0
D038	Pyridine.....	110-86-1	\3\ 5.0
D010	Selenium.....	7782-49-2	1.0
D011	Silver.....	7440-22-4	5.0
D039	Tetrachloroethylene.....	127-18-4	0.7
D015	Toxaphene.....	8001-35-2	0.5
D040	Trichloroethylene.....	79-01-6	0.5
D041	2,4,5-Trichlorophenol.....	95-95-4	400.0
D042	2,4,6-Trichlorophenol.....	88-06-2	2.0
D017	2,4,5-TP (Silvex).....	93-72-1	1.0
D043	Vinyl chloride.....	75-01-4	0.2

\1\ Hazardous waste number.
\2\ Chemical abstracts service number.
\3\ Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.
\4\ If o-, m-, and p-Cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level of total cresol is 200 mg/L.

Attachment 20.2
Extraction Fluid #1 Logbook Example

TriMatrix Laboratories, Inc.

SPLP Extraction Fluid #1
pH=4.20±0.05

Batch I.D. _____ **Date Made** _____ **Analyst** _____
Amount/Lot # H2SO4 Used ____/_____ **Amount/Lot # HNO3 Used** ____/_____
Amount 6g H2SO4/4g HNO3 Used _____ **Amount of Reagent H2O Used** _____
Total Liter Amount of Batch _____

Initial pH of Batch _____ **pH Meter Used/Date Calibrated** _____

Additional pH Readings*/Date Rechecked/Analyst/pH meter used/Date Calibrated
_____/_____/_____/_____
_____/_____/_____/_____
_____/_____/_____/_____

SPLP Extraction Fluid #1
pH=4.20±0.05

Batch I.D. _____ **Date Made** _____ **Analyst** _____
Amount/Lot # H2SO4 Used ____/_____ **Amount/Lot # HNO3 Used** ____/_____
Amount 6g H2SO4/4g HNO3 Used _____ **Amount of Reagent H2O Used** _____
Total Liter Amount of Batch _____

Initial pH of Batch _____ **pH Meter Used/Date Calibrated** _____

Additional pH Readings*/Date Rechecked/Analyst/pH meter used/Date Calibrated
_____/_____/_____/_____
_____/_____/_____/_____
_____/_____/_____/_____

SPLP Extraction Fluid #1
pH=4.20±0.05

Batch I.D. _____ **Date Made** _____ **Analyst** _____
Amount/Lot # H2SO4 Used ____/_____ **Amount/Lot # HNO3 Used** ____/_____
Amount 6g H2SO4/4g HNO3 Used _____ **Amount of Reagent H2O Used** _____
Total Liter Amount of Batch _____

Initial pH of Batch _____ **pH Meter Used/Date Calibrated** _____

Additional pH Readings*/Date Rechecked/Analyst/pH meter used/Date Calibrated
_____/_____/_____/_____
_____/_____/_____/_____
_____/_____/_____/_____

*If pH is out of the acceptable range, note it and make a new batch of fluid.

file: splp1.xls — page: 1 of 50 — revision: 1.0

Attachment 20.3
Extraction Fluid #2 Logbook Example

TriMatrix Laboratories, Inc.

SPLP Extraction Fluid #2
pH=5.00±0.05

Batch I.D. _____ **Date Made** _____ **Analyst** _____
Amount/Lot # H2SO4 Used_____/_____ **Amount/Lot # HNO3 Used**_____/_____
Amount 6g H2SO4/4g HNO3 Used_____ **Amount of Reagent H2O Used**_____
Total Liter Amount of Batch_____

Initial pH of Batch_____ **pH Meter Used/Date Calibrated**_____

Additional pH Readings*/Date Rechecked/Analyst/pH meter used/Date Calibrated
_____/_____/_____/_____
_____/_____/_____/_____
_____/_____/_____/_____
_____

SPLP Extraction Fluid #2
pH=5.00±0.05

Batch I.D. _____ **Date Made** _____ **Analyst** _____
Amount/Lot # H2SO4 Used_____/_____ **Amount/Lot # HNO3 Used**_____/_____
Amount 6g H2SO4/4g HNO3 Used_____ **Amount of Reagent H2O Used**_____
Total Liter Amount of Batch_____

Initial pH of Batch_____ **pH Meter Used/Date Calibrated**_____

Additional pH Readings*/Date Rechecked/Analyst/pH meter used/Date Calibrated
_____/_____/_____/_____
_____/_____/_____/_____
_____/_____/_____/_____
_____

SPLP Extraction Fluid #2
pH=5.00±0.05

Batch I.D. _____ **Date Made** _____ **Analyst** _____
Amount/Lot # H2SO4 Used_____/_____ **Amount/Lot # HNO3 Used**_____/_____
Amount 6g H2SO4/4g HNO3 Used_____ **Amount of Reagent H2O Used**_____
Total Liter Amount of Batch_____

Initial pH of Batch_____ **pH Meter Used/Date Calibrated**_____

Additional pH Readings*/Date Rechecked/Analyst/pH meter used/Date Calibrated
_____/_____/_____/_____
_____/_____/_____/_____
_____/_____/_____/_____
_____

*If pH is out of the acceptable range, note it and make a new batch of fluid.

file: splp2.xls page: 1 of 50 revision: 1.0

Attachment 20.4
Extraction Fluid #3 Logbook Example

TriMatrix Laboratories, Inc.

SPLP Extraction Fluid #3
Reagent Water

Batch I.D. _____ **Date Made** _____ **Analyst** _____

Amount of Reagent Water Used _____

Initial pH of Batch _____ **pH Meter Used/Date Calibrated** _____

Additional pH Readings*/Date Rechecked/Analyst/pH meter used/Date Calibrated

_____ / _____ / _____ / _____ /
_____ / _____ / _____ / _____ /
_____ / _____ / _____ / _____ /

SPLP Extraction Fluid #3
Reagent Water

Batch I.D. _____ **Date Made** _____ **Analyst** _____

Amount of Reagent Water Used _____

Initial pH of Batch _____ **pH Meter Used/Date Calibrated** _____

Additional pH Readings*/Date Rechecked/Analyst/pH meter used/Date Calibrated

_____ / _____ / _____ / _____ /
_____ / _____ / _____ / _____ /
_____ / _____ / _____ / _____ /

SPLP Extraction Fluid #3
Reagent Water

Batch I.D. _____ **Date Made** _____ **Analyst** _____

Amount of Reagent Water Used _____

Initial pH of Batch _____ **pH Meter Used/Date Calibrated** _____

Additional pH Readings*/Date Rechecked/Analyst/pH meter used/Date Calibrated

_____ / _____ / _____ / _____ /
_____ / _____ / _____ / _____ /
_____ / _____ / _____ / _____ /

*If pH is out of the acceptable range, note it and make a new batch of fluid.

file: splp3.xls | page: 8 of 50 | revision: 1.0

Approved By: A 1-8-09 **QA Officer** **Approved By:** HAS 01/13/09 **Area Supervisor**

Attachment 20.5
Extraction Worksheet Example, Page 1

TriMatrix Laboratories, Inc. **SPLP Extraction Worksheet**

	Client			
	Sample Number			
1.0	Sample Description (Liquid, solid, multi-phasic)			

% Solids Determination

- **All samples must undergo % solids determination. Only re-use the solids from this section for the fluid determination. Discard any other solids/filtrates from this section!**

2.1	Analyst /Date	/	/	/	/
2.2		g	g	g	g
2.3		g	g	g	g
	Particle Size Reduction (Y/N)	Y N	Y N	Y N	Y N
2.4		g	g	g	g
2.5	Actual Sample Weight (100g min.)	g	g	g	g
2.6	Total Volume Filtrate(s)	mL	mL	mL	mL

Label the phases of the same number, A=Aqueous, B=Oil, C=Organic Phase, D= Other Phase. Make sure ALL Lab areas are aware of any Multi-phasic samples!

Phase A:	Density/Volume	d= / mL	d= / mL	d= / mL	d= / mL
Phase B:	Density/Volume	d= / mL	d= / mL	d= / mL	d= / mL
Phase C:	Density/Volume	d= / mL	d= / mL	d= / mL	d= / mL
Phase D:	Density/Volume	d= / mL	d= / mL	d= / mL	d= / mL

2.7	Weight Of Wet Solids (Filter paper wt. + wet solids)	g	g	g	g
2.8	% Wet Solids {(wt. wet solids- wt. filter paper)/ act. samp. wt.} x100	%	%	%	%

- If % wet solids, are >0.5%, but < 100%, then use equation: (100g/ % wet solids) x 100 to determine the actual amount of sample to set up the SPLP in Section 4.3. Also, do the % dry solids to complete all sample records
- If sample is 100% solid, proceed to Section 4.2. If sample is oily and % wet solids are low, then proceed with the % dry solids.

2.9	Weight of Dry Solids (Wt. of filter paper + dry solids)	g	g	g	g

- **Sample must be dried at 100C +/- 20C for two readings within +/- 1%.**

2.10	% Dry Solids {(wt. dry solids- wt filter paper)/Act. samp. wt. } x100	%	%	%	%

-If % dry solids are <0.5%, then the filtrate = the SPLP leachate. Sample is 100% liquid. Filter enough sample for all lab areas (see Section 6.3.4 for actual amounts).

-If the sample is oily, the % dry solids are low but not <0.5%, and if there are no "visible " solids on the filter paper, then the oil filtrate = the SPLP leachate (since there is only oil caught in the filter paper.)

Make sure all lab areas receive adequate aliquots of filtrate: Metals-40 mL vial, Prep Lab-40 mL vial. PLEASE, record in Narrative (Section 7) that sample was oily and filtrate=SPLP leachate.

Fluid Determination

3.1	Analyst / Date	/	/	/	/
3.2	Particle Size Reduction (Y/N). If No, explain in Narrative, Section 7	Y N	Y N	Y N	Y N

3.3 To determine what SPLP fluid to use, follow these guidelines:

- 3.3.1 - for samples taken east of the Mississippi River and for wastes/wastewaters, use SPLP fluid #1.
- 3.3.2 - for samples taken west of the Mississippi River, use SPLP fluid #2.
- 3.3.3 - for samples containing cyanide and for volatiles, use SPLP fluid #3.
- 3.3.4 - or check for a client specific fluid request.

3.4	Record Extraction Fluid Type (1, 2 or 3)	1 2 3	1 2 3	1 2 3	1 2 3
3.5					
3.6	Date Calibrated				

file: SPLPLOGp1 — page: 1 of 50 — revision: 1.0

Approved By: [signature] 1-8-09 — **QA Officer**

Approved By: MAS 01/13/09 — **Area Supervisor**

Attachment 20.6
Extraction Worksheet Example, Page 2

TriMatrix Laboratories, Inc. **SPLP Extraction Worksheet**

Sample Number				
Sample Size For SPLP Set-up				
4.1 For 100% solid sample, weight used (100 g minimum)	g	g	g	g
4.2 If % solids were >0.5% and <100%, then record:				
4.2.1 Adjusted amount of sample to yield 100g (from Section 2.)	g	g	g	g
4.2.2 Actual weight of sample (sample - weight of filter papers)	g	g	g	g
4.2.3 Total Amount of Miscible Filtrate(s) (from Section 2.6.)	mL	mL	mL	mL
4.3 For 100% liquid sample, record filtrate volumes for all lab areas in Section 6.3.4	ml	ml	ml	ml
4.4 Particle Size Reduction (Y/N)	Y N	Y N	Y N	Y N
Amount of Extraction Fluid (added by weight) For SPLP Set-up.				
5.1 Extraction Fluid (1, 2 or 3) and Batch I.D.	EF	EF	EF	EF
5.2 pH of Extraction Fluid	pH	pH	pH	pH
5.3 20 x Actual solid weight (from Section 4.1 or 4.2.2)	g	g	g	g
SPLP Extraction Record				
6.1 Analyst @ set-up/ Date (MM-DD-YY)	/	/	/	/
6.1.1 Initial Temperature @ set-up (23+/- 2 C)	C	C	C	C
6.1.2 Tumbler I.D. / RPM (30+/-2 RPM)				
6.2 Tumbling Times				
6.2.1 Time started				
6.2.2 Time completed				
6.3 Analyst @ completion/ Date (MM-DD-YY)	/	/	/	/
6.3.1 Final Temperature @ completion (23+/-2 C)	C	C	C	C
6.3.2 Initial miscible phase added back to filtered leachate(Y/N). If N, explain in section 7.0	Y N	Y N	Y N	Y N
6.3.3 Final pH of leachate (Not preserved)				
6.3.3.1 pH meter I.D.				
6.3.3.2	/	/	/	/
6.3.4 Final Volume of Leachate Collected (mL)	mL	mL	mL	mL
6.3.4.1 Metals Lab (normal aliquot =1L ; min aliquot =200 mL)	mL	mL	mL	mL
6.3.4.2 Prep Lab (normal aliquot=500 mL to 1L ; min aliquot = 500mL)	mL	mL	mL	mL
6.3.4.3 Inorganic Lab (Check with Supervisor for aliquot amount)	mL	mL	mL	mL
6.3.5 Volume of non-miscible phase collected (see Section 2.6)	mL	mL	mL	mL
6.3.5.1 Metals Lab (normal aliquot= 20 mL)	mL	mL	mL	mL
6.3.5.2 Prep Lab (normal aliquot = 40 mL)	mL	mL	mL	mL
6.3.5.3 Inorganic Lab (Check with Supervisor for aliquot amount)	mL	mL	mL	mL
6.3.6 Metals Only:				
6.3.6.1 Analyst/ Date	/	/	/	/
6.3.6.2 Metals spikes used, please list				
6.3.6.3 Preservation (pH < 2), Record actual pH	pH	pH	pH	pH

7.0 Narratives/ Comments:

file: SPLPLOGp2 — page: 2 of 50 — revision: 1.0

Approved By: [signature] 1-8-09 — **QA Officer**

Approved By: HAS 01/13/09 — **Area Supervisor**

Attachment 20.7
Extraction Worksheet Example for ZHE, Page 1

TriMatrix Laboratories, Inc. **ZHE Extraction Worksheet**

Client				
Sample Number				
1.0 Sample Description (Liquid, solid, multi-phasic)				
1.1 TCLP or SPLP				
% Solids Determination				
All samples must undergo % solids determination.				
2.1 Analyst /Date	/	/	/	/
2.2	g	g	g	g
2.3	g	g	g	g
Particle Size Reduction (Y/N)	Y N	Y N	Y N	Y N
2.4	g	g	g	g
2.5 Actual Sample Weight (25.0g min.)	g	g	g	g
2.6 Total Volume Filtrate(s)	mL	mL	mL	mL
Label the phases of the same number, A=Aqueous, B=Oil, C=Organic Phase, D= Other Phase. Make sure Volatile Lab area is aware of any Multi-phasic samples!				
Phase A: Density/Volume	d= / mL	d= / mL	d= / mL	d= / mL
Phase B: Density/Volume	d= / mL	d= / mL	d= / mL	d= / mL
Phase C: Density/Volume	d= / mL	d= / mL	d= / mL	d= / mL
Phase D: Density/Volume	d= / mL	d= / mL	d= / mL	d= / mL
2.7 Weight Of Wet Solids (Filter paper wt. + wet solids)	g	g	g	g
2.8 % Wet Solids {(wt. wet solids- wt. filter paper)/ act. samp. wt.} x100	%	%	%	%

- If % wet solids, are >0.5%, but < 100%, then use equation: (100g/ % wet solids) x 100 to determine the actual amount of sample to set up the ZHE in Section 3.2.1. Also, do the % dry solids to complete all sample record
- If sample is 100% solid, proceed to Section 4.2. If sample is oily and % wet solids are low, then proceed with the % dry solids.

2.9 Weight of Dry Solids (Wt. of filter paper + dry solids)	g	g	g	g
- Sample must be dried at 100C +/- 20C for two readings within +/- 1%.				
2.10 % Dry Solids {(wt. dry solids- wt filter paper)/Act. samp. wt. } x100	%	%	%	%

-If % dry solids are <0.5%, then the filtrate = the ZHE leachate. Sample is 100% liquid.

-If the sample is oily, the % dry solids are low but not <0.5%, and if there are no "visible " solids on the filter paper, then the oil filtrate = the ZHE leachate (since there is only oil caught in the filter paper.) PLEASE, record in Narrative (Section 7) that sample was oily and filtrate=ZHE leachate.

Approved By: 1-8-09 **QA Officer** **Approved By:** MAS 01/13/09 **Area Supervisor**

Attachment 20.8
Extraction Worksheet Example for ZHE, Page 2

TriMatrix Laboratories, Inc. **ZHE Extraction Worksheet**

Sample Number				
Sample Size For ZHE Set-up				
3.1 For 100% solid sample, weight used (25.0g minimum)	g	g	g	g
3.2 If % solids were >0.5% and <100%, then record:				
3.2.1 Adjusted amount of sample to yield 25.0g (from Section 2.)	g	g	g	g
3.2.2 Total Amount of Miscible Filtrate(s) (from Section 2.6.)	mL	mL	mL	mL
3.3 Particle Size Reduction (Y/N)	Y N	Y N	Y N	Y N
Amount of Extraction Fluid (added by weight) For ZHE Set-up.				
4.1 Extraction Fluid for ZHE and Batch I.D -TCLP-extraction fluid I -SPLP extraction fluid, splp III (ASTM II)	EF	EF	EF	EF
4.2 pH of Extraction Fluid	pH	pH	pH	pH
4.3 pH meter used				
4.4 Date calibrated				
4.5 20 x Actual solid weight (from Section 3.1)	g	g	g	g
ZHE Extraction Record				
5.1 Analyst @ set-up/ Date (MM-DD-YY)	/	/	/	/
5.1.1 Initial Temperature @ set-up (23+/- 2 C)	C	C	C	C
5.1.2 Tumbler I.D. / RPM (30+/-2 RPM)				
5.1.3 Pressure (PSI)				
5.2 Tumbling Times				
5.2.1 Time started				
5.2.2 Time completed				
5.3 Analyst @ completion/ Date (MM-DD-YY)	/	/	/	/
5.3.1 Final Temperature @ completion (23+/-2 C)	C	C	C	C
5.3.2 Initial miscible phase added back to filtered leachate(Y/N). If Y, explain in section 7.0	Y N	Y N	Y N	Y N
5.3.3 Final pH of leachate (Not preserved)				
5.3.3.1 pH meter I.D.				
5.3.3.2	/	/	/	/

6.0 Narratives/ Comments: _____

file: ZHElogp2 — page: 24 of 50 — revision: 1.0

Approved By: 1-8-09 **QA Officer** — **Approved By:** HAS 01/13/09 **Area Supervisor**

Attachment 20.9
United States Environmental Protection Agency Memorandum 35, page 10

US Environmental Protection Agency Memorandum #35, Page 10

Oily Waste Analysis

One of the most frequently asked questions on the HICE Service concerns the application of the TCLP, Method 1311, to oily wastes. Many callers request technical guidance on the extraction of oily wastes due to the difficulty in the filtration on these types of waste. In many cases, an oily waste does not filter completely due to premature clogging of the glass fiber filter. This can result in the retention of standing liquid on the glass fiber filter. Material that do not pass through the glass fiber filter at the conclusion of the filtration step is defined by the method as the solid phase of the waste. The solid phase is then subjected to the leaching procedure of the TCLP. For oily wastes, clogging of the glass fiber filter can result in an overestimation of the amount of solid material available for leaching.

To solve this problem, the Agency recommends a conservative approach, one that probably will overestimate the amount of leaching. Rather than performing the TCLP extraction on the unfiltered portion of the oily waste, assume the waste is 100% liquid (e.g., will pass through the glass fiber filter) and perform a totals analysis on the oily waste to determine if the oil exceeds the appropriate regulatory level.

Filterable waste oil generated during the TCLP must be analyzed for a variety of organic and inorganic analytes. The OSW recognizes the difficulty in achieving acceptable performance for the analysis of waste oil using methods currently provided in SW-846. As a result, the Agency will provide several new methods for the preparation and analysis of oil samples to the Organic Methods Workgroup in July. In addition, a microwave assisted digestion procedure should improve the analysis of metals and will be proposed as part of the Second Update of the Third Edition of SW-846. Brief descriptions of these techniques are provided below, for additional information on the organic procedures contact Barry Lesnik at (202) 260-7459. For additional information on microwave digestion contact Ollie Fordham (202) 260-4778.

The use of purge-and-trap (Method 5030) for volatiles in oil generally results in severe contamination of analytical instrumentation. Traps, transfer lines and chromatography columns may become contaminated with oil. This leads to elevated baselines, hydrocarbon background in subsequent analyses, and cross-contamination. Headspace (Method 3810) is currently allowed only as a screening procedure in SW-846. The Agency is evaluating the use of headspace in conjunction with isotope dilution mass spectrometry for the quantitative analysis of volatiles in oil. Headspace reduces interference problems encountered with purge-and-trap. However, headspace quantitation can be questionable because the distribution of analytes is not

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TriMatrix Laboratories, Inc.

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STANDARD OPERATING PROCEDURE

Inductively Coupled Plasma Atomic Emission Spectroscopy
Perkin Elmer Optima-3000/3300DV/5300DV

SW-846 Method 6010C

APPROVALS:

Area Supervisor: Denise Coffey Date: 1-19-09
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Operations Manager: Jeff Glaser Date: 1/19/09
Jeff P. Glaser

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By: Denise S. Coffey

Total Number of Pages: 47

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma atomic emission spectroscopy (ICP) determines a wide range of elements in solution.

1.2 The procedure is applicable to a variety of matrices, including but not limited to soil, water, TCLP leachates, EPTOX leachates, SPLP leachates, ASTM leachates, oil, solvents, paint, sludge, pure product or any other matrix that may be extracted or dissolved into an acidic aqueous solution.

1.3 Most matrices require solubilization and/or digestion prior to ICP analysis.

2.0 PRINCIPLE METHOD REFERENCES

2.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Method 6010C, "Inductively Coupled Plasma-Atomic Emission Spectrometry", Revision 3, February 2007

2.2 *ICP Winlab Software Guide*, Revision E, June 1997

2.3 *Optima 3000 Family Hardware Guide*, Release B, August 1997

3.0 SUMMARY OF PROCEDURE

3.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods. Refer to the appropriate SW-846 3000 series methods for this procedure.

3.2 This procedure describes the simultaneous, multi-elemental determination of elements by ICP. The procedure measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the argon plasma torch via an argon carrier gas. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by an eschelle grating polychrometer, and the intensities are monitored by a Segmented Charge Coupled Device (SCD).

3.3 Tables 1 and 1A specify applicable elements, primary wavelengths, and reporting limits. The wavelengths listed in these tables have been selected because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity, and are treated with the same corrective techniques for spectral interference. Other elements may be added as more information becomes available, and as required.

3.4 Quantitation limits are sample dependent and may vary as the sample matrix varies; the quantitation limits provided in Tables 1 and 1A are the current nominal limits for relatively interference-free aqueous and soil matrices. These limits may need to be elevated for more complex sample matrices.

3.5 Scandium (Sc) and Yttrium (Y) are used as internal standards and are not of interest at the quantitation limit. Background correction is required for trace element determination. Background intensities must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity must be free from spectral interferences, and reflect the same change in background intensity that

occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

3.5.1 Refer to Attachment 23.1, Table 1, Analytical Wavelenths and Instrumental Reporting Limits for the Optima 3000.

3.5.2 Refer to Attachment 23.2, Table 1A, Analytical Wavelengths and Viewing for Optima 3300DV.

4.0 PARAMETER OR COMPOUND LIST

4.1 This procedure may be used for the analysis of the following metals:

Aluminum	Molybdenum
Antimony	Nickel
Arsenic	Phosphorus
Barium	Potassium
Beryllium	Selenium
Boron	Silicon
Cadmium	Silver
Calcium	Sodium
Cerium**	Strontium
Chromium	Sulfur *
Cobalt	Thallium
Copper	Tin
Iron	Titanium
Lead	Vanadium
Lithium	Zinc
Magnesium	
Manganese	

* Optima 3300DV and 5300DV only
**For interference correction only.

5.0 REFERENCED SOPs

5.1 TriMatrix SOP GR-15-102, *Laboratory Waste Disposal,* latest revision

5.2 TriMatrix SOP GR-01-137, *Acid Digestion of Sediments, Sludges and Soils Using Block Digestion,* latest revision

5.3 TriMatrix SOP GR-01-147, *Acid Digestion of Wastewater, Dissolved Water, Total Water and Extracts, using Block Digestion for the ICP Analysis of Total Metals,* latest revision

5.4 TriMatrix SOP GR-01-119, *Toxicity Characteristic Leaching Procedure (TCLP),* latest revision

5.5 TriMatrix SOP GR-01-117, *Synthetic Precipitation Leaching Procedure (SPLP),* latest revision

5.6 TriMatrix SOP GR-10-123, *Element™ Data Transfer and Review*, latest revision

5.7 TriMatrix SOP GR-10-125, *Method Detection Limit (MDL)*, latest revision

6.0 INTERFERENCES AND CORRECTIVE PROCEDURES

6.1 Spectral Interferences

6.1.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements.

6.1.2 Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

6.1.3 Users of simultaneous multi-element instruments, such as the Optima 3000, 3300DV and 5300DV must verify the absence of spectral interference at the analytical wavelength. As an example, Table 2 (Refer to Attachment 23.3, Table 2, Analyte Emission Equivalents Arising from Interference for the Optima 3000, Instrument 101) shows the interferences that have been documented for the Optima 3000. The data in Table 2 is intended as rudimentary guides for indicating potential interferences. This data will periodically change; therefore, these values are only guides. Interelement correction factors are re-evaluated every six months, or following major instrument maintenance, whichever is more frequent.

6.1.3.1 The interference is expressed as apparent false concentration per ppm of interferent. The instrument software automatically calculates and compensates for interelement corrections (IEC). For more information on the topic of interelement corrections, refer to the Optima 3000, Optima 3300DV or Optima 5300DV software manuals.

6.1.3.2 The dashes in Table 2 indicate that no measurable interferences were observed at the concentrations used to create this table.

6.1.4 Interelement interference check solution elements are selected based on the target analyte or analytes interfered with.

6.1.4.1 For example, iron interferes with beryllium and is included in solution IFB-1. Titanium interferes with thallium and is included in solution IFB-2.

6.1.4.2 Multiple elements that interfere with a target analyte are in the solution where the highest degree of interference can be evaluated. For example, copper, iron, manganese, nickel and vanadium interfere with antimony. Iron is in IFB-1 and the rest are in IFB-2 so antimony is in IFB-2.

6.1.4.3 To further validate interelement correction factors, all elements are monitored in each IFA solution if a false positive or negative greater then twice the analyte

reporting limit is observed. If any are observed, locate and correct the problem before reporting analyte results.

6.2 Physical Interferences

6.2.1 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations due to a decrease in nebulization and transport efficiencies. Both the Optima 3000 and 3300DV compensate for the viscosity and solids content by using on-line internal standard addition. The internal standards, in this case Sc and Y, are added via a peristaltic pump to the sample stream as it is pumped into the plasma. If the internal standard intensity changes in a sample relative to a standard, the data for that sample is electronically altered to reflect the assumed change in analyte intensity.

6.2.2 Samples containing large amounts of elements may decrease the forward power available to the plasma for elemental excitation. The RF generator used by Perkin Elmer in both the Optima 3000 and 3300DV is a free running generator, meaning that the generator may compensate for a decrease in the forward power by increasing the amount of power to the RF coil. The result of this compensation is that the forward power available to the plasma will remain at the set level if large quantities of analytes are introduced into the system.

6.2.3 The Optima 3000, 3300DV and 5300DV use a mass flow control for the argon supply which has been reported to improve instrument performance.

6.3 Chemical Interferences

6.3.1 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique.

6.3.2 If observed, chemical interferences can be minimized as follows:

6.3.2.1 By careful selection of operating conditions such as incident power and/or observation position

6.3.2.2 By buffering the sample

6.3.2.3 By matrix matching

6.3.2.4 By using the method of standard additions

6.3.3 Chemical interferences are highly dependent on matrix type and the specific element.

7.0 SAFETY PRECAUTIONS

7.1 The analyst must comply with all standard operating procedures for health and safety as outlined in the TriMatrix Laboratories, Inc. Laboratory Safety Manual.

7.2 Concentrated acids are used in the preparation of standards and samples for analysis by ICP. Gloves, labcoats, and safety glasses must be worn at all times when handling concentrated acids. Gloves must also be worn when handling samples. Refer to the Material Safety Data Sheets (MSDS) for information on these or any other chemicals utilized in this procedure.

7.3 Check the exhaust hood over the instrument to be sure it is operating correctly. If the ventilation system is not working properly, extinguish the plasma and immediately contact the metals lab supervisor. Under no circumstances should the ICP be used if the exhaust hood is not working.

7.4 The plasma emits UV radiation. Avoid looking directly at the plasma without some type of strong UV protection. The instrument uses a UV resistant material in the viewing port so the analyst may watch the plasma. Do not tamper with this plate. Do not operate the instrument without this plate in place. Do not attempt to view the plasma directly or indirectly in any way. Failure to follow this policy may cause very serious and immediate damage to the retina of the eye.

7.5 The ICP emits a strong RF field. To minimize exposure to this field, Perkin Elmer has included several safety interlocks to prevent exposure of the analyst to harmful radiation. Never override any interlock on the ICP. When working on the instrument, always replace all of the RF shielding using all of the supplied screws. If any safety device has been tampered with, contact the metals lab supervisor.

7.6 The ICP uses argon to sustain the plasma and to nebulize the sample into the plasma. Although argon in and of itself is not hazardous or flammable, it may cause suffocation through oxygen deprivation. It is therefore imperative that all sources of argon be turned off at the valve when not in use. Since argon is colorless and odorless, if you feel lightheaded, evacuate the metals lab at once and notify the metals lab supervisor.

7.7 Many of the chemicals and elements used in this procedure are toxic if ingested. Refer to the MSDS for information on these or any other chemicals utilized in this procedure.

7.8 No food or drink is allowed in the metals lab. Food or drink may become contaminated with acid or metals and may therefore be hazardous.

7.9 Wash hands before starting work. Chemicals may be present on the skin which may interfere with metals analysis. Wash hands before leaving the metals lab. Chemicals and acids may be on the skin which could eventually be ingested or passed on to a third party through casual contact.

8.0 SAMPLE SIZE, COLLECTION, PRESERVATION AND HANDLING PROCEDURES

8.1 Aqueous samples must have been acidified at the time of collection to a pH of <2. If the pH is not <2 when received by the laboratory, the sample pH must be lowered to <2 during the sample receipt process. A minimum of 24 hours must elapse after adjustment prior to sample digestion.

8.2 Solid samples require no preservation for metals. However, if the same sample container is scheduled for other analyses where refrigeration of the sample is needed, store the sample at 4 ±2° C.

8.3 Samples may be collected in glass or plastic. If Silicon or Boron is to be analyzed, plastic containers must be used. The acidified sample must never come into contact with any metal as this would cause leaching of the metal into the sample.

8.4 For the analysis of dissolved metals, the sample must have been filtered on site and then acidified to pH <2. If the pH was not <2, the sample pH must be lowered to <2 during the sample receipt process and a minimum of 24 hours must elapse after adjustment prior to sample analysis.

8.5 Hold times for all metals for ICP analysis is 180 days. In the case of TCLP or similar leachates, the hold time starts once leachate generation has been completed.

8.6 The minimum sample size for this procedure is 50 mL and 150 mL if samples require Matrix QC. Soils, sediments, and solid waste samples require a minimum of 50 g of sample. This implies that the sample must be solubilized prior to analysis. A smaller minimum amount may be used if the sample may be diluted at the sacrifice of the quantitation limit.

8.7 Digested (solubilized) samples and undigested acidified aqueous samples need not be refrigerated. All samples and digestates must be at room temperature before analysis.

9.0 INSTRUMENTATION, APPARATUS, AND MATERIALS

9.1 Inductively coupled argon plasma emission spectrometer:

9.1.1 Optima 3000/3300DV/5300DV Inductively Coupled Plasma Optical Emission Spectrometer with an Eschelle based polychrometer and a Segmented-Array Charge-Coupled-Device Detector (SCD). The instrument is capable of taking readings in the UV/VIS spectrum with a wavelength range of 167 to 782 nm. The RF generator employed runs at 40 MHz.

Operating conditions: The analyst must follow the instructions provided by the instrument's manufacturer. For operation with organic solvents, the use of the auxiliary argon inlet is recommended, as is solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental reporting limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

9.1.2 Perkin Elmer IEEE autosampler, model AS-90/AS-91. This autosampler must be installed by a Perkin Elmer representative.

9.2 Recirculator/chiller, Polyscience 633 or equivalent. Temperature must be maintained at 18° C and pressure must be at 50 psi. The recirculator is attached directly to the instrument to maintain isothermal conditions within the optics cavity.

9.3 Computer running Perkin Elmer control software. An IBM compatible 80486SX25 or faster computer with at least 64 MB RAM, a 1G hard disk, and a VGA color monitor is needed. The current software used by the instrument is ICP Winlab software version 1.47 running in a Windows NT Environment. The software version may be updated if it performs at least as well as the older version. Major updates, such as moving to another operating platform will require an update to this procedure.

9.4 Appropriate Printer. The printer must be attached to the computer using an appropriate communication cable. Refer to the Instrument manual for further printer specifications.

9.5 15 mL clear centrifuge tubes or equivalent. The tubes must stand upright within the autosampler rack without tipping or leaning.

9.6 Autopipettors capable of delivering 50-1000 µL.

9.7 Class A volumetric flasks, various volumes.

9.8 Class A reusable pipettes, various volumes.

9.9 500 mL plastic bottles for standards and quality control.

10.0 ROUTINE PREVENTIVE MAINTENANCE

10.1 At the beginning of each shift (every 8 hours) the manifold pump tubing must be replaced. Refer to Section 15.5 for a discussion on changing the pump tubing. Update the instrument maintenance logbook.

10.2 There are 3 filters on the Optima 3000 that must be cleaned every week. The first two filters are located on the back of the instrument on the right-hand side. The third filter is located on the left.

10.2.1 Remove the filters from the holders. The right-hand filters have a cover that 'pops' off. The left-hand filter just slides up and out of its holder.

10.2.2 Wash the filters in soap and water to loosen any dirt and dust from the filters.

10.2.3 Squeeze any excess water from the filters. Dry the filters with a paper towel. Allow these filters to air dry.

10.2.4 If there are extra filters, replace the filters on the instrument, otherwise wait until the newly washed filters are dry before replacing them.

10.2.5 Place a note in the instrument maintenance logbook that the filters were cleaned.

10.3 Inspect the waste container on the floor under the instrument every shift. If the container is full, properly dispose of the liquid.

10.4 Visually inspect the torch before lighting the plasma. Do not touch or move the torch. This inspection must be visual only.

10.4.1 Open the doors to the torch chamber.

10.4.2 Observe the torch. If the torch is broken or cracked, replace it. Refer to Section 10.6 for a discussion on how to assemble and disassemble the torch.

10.4.3 Listen for any obvious leaks in the argon lines going to the torch or nebulizer. If leaks are heard, investigate them and tighten the fittings to stop the leak. If the leak cannot be found or cannot be stopped, contact the metals lab supervisor.

10.5 Once every four to eight weeks, disassemble the entire torch assembly and inspect all parts for wear. Replace all worn or damaged parts. Record all changes in the instrument maintenance logbook.

10.5.1 Inspect the drain line at the base of the spray chamber. There must be no leaks or cracks in the tubing. If a problem exists, replace the O-rings in the drain cap. Place a note in the instrument maintenance logbook that the tubing was replaced.

10.5.2 Inspect the nebulizer for wear.

10.5.14.1 Salt deposits, if present, should be removed with water.

10.5.14.2 If a cross-flow nebulizer is used, check the tips for wear. Replace the tips if excessive wear is noted. Record any actions in the instrument maintenance logbook.

10.5.3 Replace the alumina injector with a newly cleaned one. To clean dirty alumina injectors, place them in a plastic 100 mL graduated cylinder. In a hood, cover the injectors with aqua regia. Allow the injectors to soak for 2 hours. Rinse the alumina injectors with tap water, then ASTM Type II water. Place clean injectors in the appropriate drawer for future use. Record the change in the instrument maintenance logbook.

10.5.4 Check all O-rings on the alumina injector holder. Any cracked or chipped O-rings must be replaced with new ones. The book located next to the spare parts drawers has an exploded view of the torch assembly. Use this diagram to identify the exact part number needed for replacement. Note any replacements in the instrument maintenance logbook.

10.5.5 Check the torch for damage. Brown discoloration at the top of the torch is normal. Since the Optima torch has exit windows cut into the torch for light to pass through, this discoloration need not be rectified. Look at the bottom of the torch. There are frequently chips at this spot on the torch. If chips are observed, replace the torch. Never use a torch that is chipped, cracked, or broken. See the metals lab supervisor for help in replacing the torch as this procedure is beyond the scope of this SOP. Note replacement in the instrument maintenance logbook.

10.5.6 Replace the alumina injector support in the spray chamber.

10.5.7 Re-install the spray chamber and alumina injector holder unit in the quick-change mount.

10.5.8 Replace the alumina injector.

10.5.9 Replace the torch on the assembly.

10.5.10 Replace the nebulizer.

10.5.11 Replace the torch assembly on the mounting bracket.

10.5.12 Close the torch box doors.

10.5.13 Note any changes made to the torch during this procedure in the instrument maintenance logbook.

10.6 Inspect the printing quality of the printer. If the print is hard to read or light in appearance, replace the printer cartridge with the appropriate replacement.

11.0 CHEMICALS AND REAGENTS

11.1 Acids used in the preparation of standards and for sample processing must be reagent grade or better. Re-distilled acids may be used if it has been demonstrated that the acid is free from contamination.

11.1.1 Concentrated hydrochloric acid, trace metal grade (Fisher Cat #A50B-212) (or equivalent).

11.1.2 Concentrated nitric acid, trace metal grade (Fisher Cat. #A509-212) (or equivalent).

11.2 ASTM Type II water (ASTM D1193). Deionized water is fed into an all glass distillation unit from Barnstead (Model FI-STREEM 2). The resulting distillate is immediately placed into a plastic container. Impurities are measured by the Inorganics group at TriMatrix. This is the only water acceptable for use in the metals laboratory for dilutions or standard preparation.

11.3 Argon gas supply: Welding grade or better. Currently, this is plumbed from a liquid argon tank located outside of the building. Argon is used as the main plasma gas, the auxiliary plasma gas, and the nebulizer carrier gas.

11.4 Nitrogen gas supply: Currently, this is plumbed from a liquid N2 tank located outside of the building. N_2 is used to purge the optics cavity of Oxygen so that measurements below 190 nm may be made accurately.

11.5 Aqua Regia. Three parts hydrochloric to one part nitric. This is used to clean torches and alumina injectors.

12.0 STANDARDS PREPARATION

12.1 All standards are matrix matched as close to sample matrices as possible. Primary Standard stock solutions are purchased from Inorganic Ventures, Absolute Standards and/or SCP Science. All stock solutions are ICP grade single-element (1000 or 10,000 mg/L) or custom multi-element solutions at varied concentrations. All primary standards expire on the supplier's expiration date.

12.2 Secondary Standard stock solutions are purchased from other certified sources. All secondary standards expire on the supplier's expiration date.

12.3 All ICP working standards and dilutions prepared from primary standards expire 3 months after preparation or on the expiration date of the primary standard, whichever is earlier.

12.4 Current purchased custom multi-element standards include: ICP Stock A, ICP Stock B, CRL 1 Stock and

CRL 2 Stock.

12.5 Prepare the working standards.

Note: If Sulfur is a target analyte, refer to Section 12.9.

12.5.1 Rinse four clean 500 mL class A volumetric flasks with ASTM Type II water a minimum of three times.

12.5.2 Place 100 mL ASTM Type II water into each flask.

12.5.3 Pipette the correct amounts of acid into the flasks depending on the final acid concentration desired. Section 12.8.3.1 through Section 12.8.3.3 shows the acid concentrations used for matrix matching.

12.5.3.1 For 10% HCl/5% HNO_3, place 50 mL HCl into the flask and swirl. When the mixing lines are gone from solution, add 25 mL HNO_3 to the flask and swirl until the mixing lines are gone. This is for solid samples.

12.5.3.2 For 5% HCl/5% HNO_3, place 25 mL HCl into each flask and swirl. When the mixing lines are gone from solution, add 25 mL HNO_3 to each flask and swirl until the mixing lines are gone. This is for all digested aqueous samples.

12.5.3.3 For 0.5% HNO_3, place 2.5 mL HNO_3 into each flask and swirl until the mixing lines are gone. This is for non-digested aqueous samples.

12.5.4 Pipette 5.0 mL of ICP Stock A, 5.0 mL of ICP Stock B, 500 µL of 1000 mg/L Co and 500 µL of 1000 mg/L Ag into one of the flasks. This is standard four for the calibration curve.

12.5.5 Pipette 2.5 mL of ICP Stock A, 2.5 mL of ICP Stock B, 250 µL of 1000 mg/L Co and 250 µL of 1000 mg/L Ag into one of the flasks. This is standard three for the calibration curve.

12.5.6 Pipette 0.5 mL of ICP Stock A, 0.5 mL of ICP Stock B, 50 µL of 1000 mg/L Co and 50 µL of 1000 mg/L Ag into one of the flasks. This is standard two for the calibration curve.

12.5.7 Pipette 0.25 mL of CRL 1 Stock and 0.25 mL of CRL 2 Stock into one of the flasks. This is standard one for the calibration curve.

12.5.8 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.5.9 Update the standard numbers in element.

12.5.10 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents.

12.6 Sulfur working standards are prepared separately.

12.6.1 Rinse four clean 100 mL class A volumetric flasks with ASTM Type II water a minimum of three times.

12.6.2 Place 25 mL ASTM Type II water into each flask.

12.6.3 Pipette the correct amounts of acid into the flasks depending on the final acid concentration desired.

12.6.3.1 For 10% HCl/5% HNO_3, place 10 mL HCl into the flask and swirl. When the mixing lines are gone from solution, add 5 mL HNO_3 to the flask and swirl until the mixing lines are gone. This is for solid samples.

12.6.3.2 For 5% HCl/5% HNO_3, place 5 mL HCl into each flask and swirl. When the mixing lines are gone from solution, add 5 mL HNO_3 to each flask and swirl until the mixing lines are gone. This is for digested aqueous samples.

12.6.3.3 For 0.5% HNO_3, place 0.5 mL HNO_3 into each flask and swirl until the mixing lines are gone. This is for non-digested aqueous samples.

12.6.4 Pipette 500 µL of the 1000 mg/L sulfur standard into one of the flasks. This is standard 4 for the curve.

12.6.5 Pipette 250 µL of the 1000 mg/L sulfur standard into a second flask. This is standard 3 for the curve.

12.6.6 Pipette 50 µL of the 1000 mg/L sulfur standard into the third flask. This is standard 2 for the curve.

12.6.7 Pipette 10 µL of the 1000 mg/L sulfur standard into the fourth flask. This is standard 1 for the curve.

12.6.8 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.6.9 Update the standard numbers in element.

12.6.10 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents.

12.6.11 Refer to Attachment 23.6, Table 5, Optima Working Standard Concentrations.

12.7 Prepare the stock interelement check standard solutions for IFA-1, IFA-2, IFB-1, and IFB-2.

12.7.1 The solution Interf-1 is purchased from Inorganic Ventures.

12.7.2 Prepare solution ICS-1 Analytes.

12.7.2.1 Rinse a clean 100 mL class A volumetric flask with ASTM Type II water a minimum of three times.

12.7.2.2 Place 2 mL HNO_3 in the flask.

12.7.2.3 Pipette the following amounts of the standards below into the flask, swirling after each addition. Always use a new pipette for each standard and never pipette directly out of the primary standard source bottle.

12.7.2.3.1 10 mL each of 1000 mg/L Ag, Cd, Ni, Pb, Zn

12.7.2.3.2 5 mL each of 1000 mg/L Ba, Be, Co, Cr, Cu, Mn, V

12.7.2.4 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.7.2.5 Update the standard numbers in element.

12.7.2.6 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents.

12.7.3 Prepare solution IFA-2 Interferent.

12.7.3.1 Rinse a clean 100 mL class A volumetric flask with ASTM Type II water a minimum of three times. Place 10 mL HNO_3 in the flask.

12.7.3.2 Pipette the following amounts of the standards below into the flask, swirling after each addition. Always use a new pipette for each standard, and never pipet directly out of the primary standard source bottle.

10 mL each of 10,000 mg/L Cr, Cu, Mn, Ni, Ti, V

12.7.3.3 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.7.3.4 Update the standard numbers in element.

12.7.3.5 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents..

12.7.4 Prepare solution IFA-2 Analyte.

12.7.4.1 Rinse a clean 100 mL class A volumetric flask with ASTM Type II water a minimum of three times. Place 2 mL HNO_3 in the flask.

12.7.4.2 Pipette the following amounts of the standards below into the flask, swirling after each addition. Always use a new pipette for each standard and never pipet directly out of the primary standard source bottle.

12.7.4.2.1 10 mL each of 1,000 mg/L Al, As, B, Mo, Sb, Se, Tl

12.7.4.2.2 5 mL each of 10,000 mg/L Ca, Mg, Na

12.7.4.3 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.7.4.4 Update the standard numbers in element.

12.7.4.5 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents.

12.8 Prepare the interelement check standard solution IFA-1.

12.8.1 Rinse a clean 500 mL Class A volumetric flask with ASTM Type II water a minimum of three times.

12.8.2 Place about 100 mL ASTM Type II water into the flask.

12.8.3 Pipette the correct amounts of acid into the flask depending on the final acid concentration desired.

12.8.3.1 For 10% HCl/5% HNO_3. Place 50 mL HCl into the flask and swirl. When the mixing lines are gone from the solution, add 25 mL HNO_3 to the flask, and swirl until the mixing lines are gone. This is for solid samples.

12.8.3.2 For 5% HCl/5% HNO_3. Place 25 mL HCl into the flask and swirl until the mixing lines are gone from the solution. Add 25 mL HNO_3 to the flask and swirl until the mixing lines are gone from the solution. This is for digested aqueous samples.

12.8.3.3 For 0.5% HNO_3. Place 2.5 mL HNO_3 into the flask and swirl. This is for non-digested aqueous samples.

12.8.4 Pipette 10 mL of the solution Interf-1 into the flask and swirl.

12.8.5 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.8.6 Update the standard numbers in element.

12.8.7 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents.

12.9 Prepare the interelement check standard solution IFA-2.

12.9.1 Rinse a clean 500 mL Class A volumetric flask with ASTM Type II water a minimum of three times.

12.9.2 Place 100 mL ASTM Type II water into the flask.

12.9.3 Pipette the correct amount of acid into the flask depending on the final acid concentration desired.

12.9.3.1 For 10% HCl/5% HNO_3. Place 50 mL HCl into the flask and swirl until the mixing lines are gone from the solution. Add 25 mL HNO_3 to the solution. Add 25 mL HNO_3 to the flask and swirl until the mixing lines are gone. This is for solid samples.

12.9.3.2 For 5% HCl/5% HNO_3. Place 25 mL HCl into the flask and swirl until the mixing lines are gone from the solution. Add 25 mL HNO_3 to the flask and swirl until the mixing lines are gone from the solution. This is for digested aqueous samples.

12.9.3.3 For 0.5% HNO_3. Place 2.5 mL HNO_3 into the flask and swirl. This is for non-digested aqueous samples.

12.9.4 Pipette 10 mL of the solution IFA2 – Interferent into the flask.

12.9.5 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.9.6 Update the standard numbers in element.

12.9.7 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents.

12.10 Prepare the interelement check standard solution IFB-1.

12.10.1 Rinse a clean 500 mL Class A volumetric flask with ASTM Type II water a minimum of three times.

12.10.2 Place 100 mL ASTM Type II water into the flask.

12.10.3 Pipette the correct amount of acid into the flask depending on the final acid concentration desired.

12.10.3.1 For 10% HCl/15% HNO_3. Place 50 mL HCl into the flask and swirl until the mixing lines are gone from the solution. Add 25 mL HNO_3 to the solution. Add 25 mL HNO_3 to the flask and swirl until the mixing lines are gone. This is for solid samples.

12.10.3.2 For 5% HNO_3/5% HCl. Place 25 mL HCl into the flask and swirl until the mixing lines are gone. This is for solid samples.

12.10.3.3 For 0.5% HNO_3. Place 2.5 mL HNO_3 into the flask and swirl. This is for non-digested aqueous samples.

12.10.4 Pipette 10 mL of the solution Interf-1 into the flask and swirl.

12.10.5 Pipette 5 mL of the solution ICS-1 analyte into the flask and swirl.

12.10.6 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.10.7 Update the standard numbers in element.

12.10.8 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents.

12.10.9 Refer to Attachment 23.7, Table 6 IFB-1, Working Solution.

12.11 Prepare the Interelement Check solution IFB-2

12.11.1 Rinse a clean 500 mL class A volumetric flask with ASTM Type II water a minimum of three times.

12.11.2 Place 100 mL ASTM Type II water into a flask.

12.11.3 Pipette the correct amount of acid into the flask depending on the final acid concentration desired.

12.11.3.1 For 10% HCl/5% HNO_3, place 50 mL HCl into the flask and swirl. When the mixing lines are gone from the solution, add 25 mL HNO_3 to the flask, and swirl until the mixing lines are gone. This is for solid samples.

12.11.3.2 For 5% HCl/5% HNO_3, place 25 mL HCl into each flask and swirl. When the mixing lines are gone from solution, add 25 mL HNO_3 to each flask and swirl until the mixing lines are gone. This is for digested aqueous samples.

12.11.3.3 For 0.5% HNO_3, place 25 mL HNO_3 into each flask and swirl until the mixing lines are gone. This is for non-digested aqueous samples.

12.11.4 Pipette 10 mL of the solution IFA-2 interferent into the flask. Swirl the flask.

12.11.5 Pipette 5 mL of the solution IFA-2 analyte into the flask. Swirl the flask.

12.11.6 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.11.7 Update the standard numbers in element.

12.11.8 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents.

12.11.9 Refer to Attachment 23.8, Table 7, IFB-2 Working Solution.

12.12 Prepare the CRL working standard.

12.12.1 Rinse a clean 500 mL Class A volumetric flask with ASTM Type II water a minimum of three times.

12.12.2 Place about 100 mL ASTM Type II water into the flask.

12.12.3 Pipette the correct amounts of acid into the flask depending on the final acid concentration desired.

12.12.3.1 For 10% HCl / 5% HNO3. Place 50 mL HCl into the flask and swirl. When the mixing lines are gone form the solution, add 25 mL HNO3 to the flask, and swirl until the mixing lines are gone. This is for solid samples.

12.12.3.2 For 5% HCl / 5% HNO3. Place 25 mL HCl into the flask and swirl. When the mixing lines are gone from the solution, add 25 mL HNO3 to the flask and swirl until the mixing lines are gone. This is for digested aqueous samples.

12.12.3.3 For 0.5% HNO3. Place 2.5 mL HNO3 into the flask and swirl. This is for non-digested aqueous samples.

12.12.4 Pipette 0.5 mL of the CRL 1 Stock and 0.5 mL of the CRL 2 Stock into the flask.

12.11.6 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.11.7 Update the standard numbers in element.

12.11.8 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents.

12.13 Prepare the internal standard solution.

12.13.1 Rinse a clean 1000 mL Class A volumetric flask with ASTM Type II water a minimum of three times.

12.13.2 Place 100 mL ASTM Type II water into the flask.

12. 13.3 Pipette the correct amounts of acid into the flask depending on the final acid concentration desired.

12.13.3.1 For 10% HCl / 5% HNO3. Place 100 mL HCl into the flask and swirl. When the mixing lines are gone from the solution, add 50 mL HNO3 to the flask, and swirl until the mixing lines are gone. This is for solid samples.

12.13.3.2 For 5% HCl / 5% HNO3. Place 50 mL HCl into the flask and swirl. When the mixing lines are gone from the solution, add 50 mL HNO3 to the flask and swirl until the mixing lines are gone. This is for digested aqueous samples.

12.13.3.3 For 0.5% HNO3. Place 5.0 mL HNO3 into the flask and swirl. This is for non-digested aqueous samples.

12.13.4 Use the volumes listed to prepare concentrations for the instrument being used:

12.13.4.1 Pipette 0.50 mL of 1000 mg/L Sc stock standard and 1.0 mL of 1000 mg/L Y stock standard into the flask for the Optima 3000.

12.13.4.2 Pipette 2.0 mL of 1000 mg/L Sc stock standard and 0.075 mL of 1000 mg/L Y stock standard into the flask for the Optima 3300DV.

12.13.4.3 Pipette 2.0 mL of 1000 mg/L Sc stock standard and 0.34 mL of 1000 mg/L Y stock standard into the flask for the Optima 5300DV.

12.13.5 Dilute each flask to the volumetric mark with ASTM Type II water and mix well. Do not transfer to bottles. Adding the water generates heat and a final volume adjustment must be made after the flasks return to room temperature.

12.13.6 Update the standard numbers in element.

12.13.7 After the final volume adjustment, pour the flask contents into clean bottles and label to describe each bottle's contents.

12.14 Prepare the Secondary Calibration Verification (SCV)

12.14.1 There are two SCV stock solutions currently being purchased from Environmental Express.

12.14.1.1 QC Solution A:

12.14.1.1.1 500 mg/L of Al, As, P, Tl, Se

12.14.1.1.2 1000 mg/L each of Ca, K, Mg, Na

12.14.1.1.3 100 mg/L each of V, Ba, B, Cu, Fe, Li, Zn, Cd, Cr, Co, Pb, Mn, Ni, Sr

12.14.1.1.4 10 mg/L of Be

12.14.1.2 QC Solution B:

12.14.1.2.1 500 mg/L of Sb, Sn, Si

12.14.1.2.2 100 mg/L each of Ag, Mo, Ti

12.17.2 The working SCV is prepared fresh daily.

12.17.2.1 Pipet 50 µL of each SCV stock into 9.9 mL of 10% HCl/5% HNO_3 reagent blank. This is for solid samples.

12.17.2.2 Pipet 50 µL of each SCV stock into 9.9 mL of 5% HCl/5% HNO_3 reagent blank. This is for digested aqueous samples.

12.17.2.3 Pipet 50 µL of each SCV stock into 9.9 mL of 0.5% HNO_3 reagent blank. This is for non-digested aqueous samples.

12.17.3 Refer to Attachment 23.12, Table 11, SCV Concentration when diluted according to instructions.

13.0 SAMPLE PREPARATION

13.1 Soil, sludge, oil and waste samples must be digested prior to analysis. Refer to TriMatrix SOP GR-01-137 for the digestion procedure.

13.2 Leachates, such as from the TCLP or SPLP extraction, must be digested. Refer to TriMatrix SOPs GR-01-119, GR-01-117, and GR-01-147 for extraction and digestion.

13.3 Water and groundwater samples for total metals must be digested. Refer to TriMatrix SOP GR-01-147 for the digestion.

14.0 CALIBRATION PROCEDURES

14.1 The Optima 3000, 3300DV and 5300DV must be calibrated for every analytical run or every 24 hours, whichever is more frequent.

14.1.1 Before analysis can begin, the instrument must be profiled using a 10 mg/L Mn solution.

14.1.1.1 Click on the tools drop down menu, then spectrometer control.

14.1.1.2 Aspirate the 10 mg/L Mn solution.

14.1.1.3 Click on "optimize".

14.1.1.4 The instrument will take several readings at different positions in the plasma path.

14.1.1.5 When readings are complete, the instrument will set the viewing position to the highest emission count.

14.1.1.6 Record the highest emission count and position setting in the maintenance logbook.

14.1.1.7 If emission readings vary by more than 30% from the recorded value due to wear or instrument maintenance, re-profile the emission output.

14.1.2 Calibration standards are prepared according to Section 12.0. The final concentrations of the working standards used to create the curve are listed in Table 5.

Note: Concentration of the lowest calibration standard must be at or below the reporting limit.

14.1.3 The mean response of a minimum of two exposures of each standard to the plasma is used in generating a calibration curve.

14.1.4 In all cases, calibration is performed using a multi-point calibration with a calculated zero intercept (not forced). The correlation coefficient must be greater than or equal to 0.995. If correlation is less than 0.995, recalibrate the instrument or postpone analysis for only out-of-control elements, until an acceptable calibration can be attained. If correlation is still less than 0.995, contact the metals laboratory supervisor for assistance.

14.2 After calibration, run an initial calibration verification

14.2.1 Analyze the secondary calibration verification (SCV). The SCV standard must be prepared from an independent (second-source) material at or near the mid-range of the calibration curve. The control window for the SCV is 90% to 110% recovery of the true value. If the percent recovery of any target analyte does not fall within the control window, reanalyze the SCV one time. If the recovery is still out of control, recalibrate the instrument and start the analysis at Section 14.2 or postpone analysis for only the out-of-control elements until an acceptable calibration can be obtained.

14.2.2 Analyze the CCB. The CCB is a reagent blank having the same acid concentration as the standards. The absolute value of the mean ICB reading must be less than the lowest reporting limit required for the analysis. If the CCB is not within the control limit, reanalyze the CCB one time. If the recovery is still out, recalibrate the instrument and start again at Section 14.2 or postpone analysis for only the out-of-control elements until an acceptable calibration can be attained.

14.2.3 Analyze the Contract Required Detection Limit (CRL). Analyze a low level standard at 2 times the standard quantitation limit. The control window is 50% to 150% recovery. If the recovery is outside of the control window, a narrative must be attached to the LIMS batch.

14.2.4 Analyze the IFA-1 solution. The IFA-1 is comprised of interfering elements only. Depending upon the analytes of interest, a second IFA-2 solution containing additional elements may also need to be analyzed. The purpose of the standard(s) is to demonstrate that, with the current interelement correction factors in place, there are no measurable spectral interferences. The QC acceptance window is 80% to 120% recovery of the true value for the elements spiked and ±2 times the reporting limit for the elements not spiked in the solution.

14.2.5 Analyze the IFB-1 solution (Interelement Correction Standard-1). The IFB-1 solution is a standard that contains four to six elements (i.e., interferents), at high concentrations with remaining elements present at trace levels. Depending upon the analytes of interest, a second IFB-2 solution containing additional elements may also need to be analyzed. The purpose of the standard(s) is to demonstrate that, with the current interelement correction factors in place, there are no measurable spectral interferences. The QC acceptance window is 80% to 120% recovery of the true value.

14.2.6 Follow analysis of the IFB standards with analysis of a Continuing Calibration Verification (CCV) standards with a concentration at the mid-point of the calibration curve. The acceptance window for this QC is 90% to 110% recovery of the true value and <5% RSD. If the CCV is not within the control limits, reanalyze the CCV one time. If the recovery is still out, recalibrate the instrument for the affected analytes and start again at Section 14.2, or postpone analysis for only the out-of-control elements until an acceptable calibration can be attained.

14.2.7 Analyze the CCB again. If the CCB is not within the control limits, reanalyze the CCB one time. If the recovery is still out, recalibrate the instrument and start again at Section 14.2, or postpone analysis for only the out-of-control elements until an acceptable calibration can be attained. All samples with an unacceptable CCB must be reanalyzed for the affected target analyte(s).

14.2.8 Analyze up to 10 samples. If the percent RSD is >20 for any result, the sample immediately prior is to be checked for a high analyte concentration. If the analyte is high, then check the replicates of the sample in question to verify the concentration is not decreasing. If the concentration is decreasing, reanalyze the sample. If the replicates are not decreasing, report the result.

14.2.9 Analyze the CCV again. If the CCV is not within the control limits, reanalyze the CCV one time. If the recovery is still out, recalibrate the instrument and start again at Section 14.2, or postpone analysis for only the out-of-control elements until an acceptable calibration can be attained. All samples with an unacceptable CCV must be reanalyzed for the affected target analyte(s).

14.2.10 Analyze the CCB again. If the CCB is not within the control limits, reanalyze the CCB one time. If the recovery is still out, recalibrate the instrument and start again at Section 14.2, or postpone analysis for only the out-of-control elements until an acceptable calibration can be attained. All samples with an unacceptable CCB must be reanalyzed for the affected target analyte(s).

14.2.11 Repeat Sections 14.2.8 through 14.2.11 until the end of the analytical run.

14.2.12 End the run with a compliant CCV and CCB analysis.

15.0 ANALYTICAL PROCEDURE

Note: The following section assumes the user is familiar with Optima 3000 and 3300DV operating software. If unfamiliar or unsure, consult the instrument manual for additional instructions.

This procedure provides adequate instruction, but is not intended to replace instrument operating manuals.

15.1 Preliminary treatment of all matrices is always necessary because of the complexity and variability of sample matrices. Digestion procedures are presented in the appropriate Sample Preparation Methods.

15.2 Turn on the instrument.

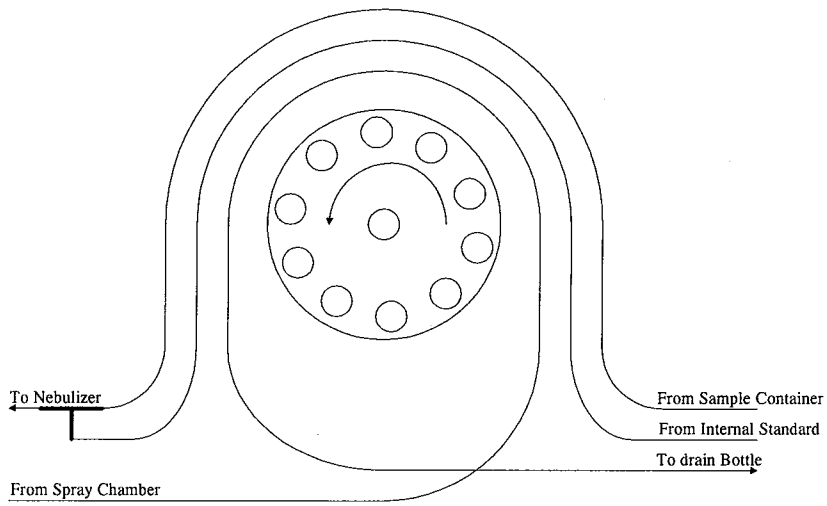
15.3 Boot the computer and ICP WinLab software.

15.4 If the instrument power or RF generator power was not on when the system was booted, an equilibration time will be required by the instrument before the plasma may be lit. The instrument software will alert the operator in this event. Wait until the instrument alerts you that it is ready before proceeding to the next step.

15.5 Change the peristaltic pump tubing. The tubing should be changed every eight hours since the tension exerted on the tubing by the pump will cause the tubing to stretch. Place the waste line on the bottom so that the pump is pumping the waste away from the ICP. Place the internal standard line in the middle so that the pump is pumping the internal standard toward the ICP. Place the sample line on the top so that the pump is pushing the sample to the ICP. Refer to Figure 1 for the correct orientation of the pump tubing. Update the instrument maintenance log to reflect that a change in the pump tubing. Currently, three types of tubing are being used:

Color	Type
Black/Black	Sample line
Orange/Green	Internal standard line
Red/Red	Waste line

Figure 1
Peristaltic Pump Setup



15.6 Recalibrate the spectrometer. The Hg recalibration helps to compensate for drift during the analysis. Although not required, this procedure will greatly increase the stability of the spectrometer, and is therefore highly recommended. Enter the spectrometer mode. Click on the Hg recalibration button. Wait until the computer states that the Hg lamp recalibration is complete. Change the Hg recal time to 2 hours.

15.7 Table 8 lists typical element file conditions for the Optima 3000. Note that any or all of the conditions listed below may change for an element if it has been established that new conditions are at least equivalent to those listed.

15.8 Refer to Attachment 23.9, Table 8, Element Conditions for the Optima 3000. Dashes indicate no Background subtraction point used for this interval.

15.9 Set up the analysis on paper using a sample identification weight sheet (ID/WT sheet). This sheet has columns where the operator enters the sample description, corresponding autosampler position number, digestion dilution (if any), and any subsequent dilutions performed on the sample. This sheet must be filled out before continuing with the procedure, as it is an integral part of the analysis. A typical starting sequence for the ID/WT sheet is given in Table 9. Consult the area supervisor if assistance is required in filling out this sheet.

15.10 Refer to Attachment 23.10, Table 9, ID/WT Sheet Setup for Instrument Calibration and Verification

15.11 Set up the analysis.

15.11.1 Import the analysis sequence from the laboratory information management system Element™ in accordance with TriMatrix GR-10-123.

15.11.2 Enter the analysis sequence.

15.11.3 Analyze samples.

15.11.4 When the analysis is complete, the autosampler will return to position "0" and wait for operator input.

16.0 CALCULATIONS AND DATA HANDLING

16.1 The concentration of each sample is read directly from the computer printout. Dilution factors should be taken into account in the sample information file.

$$C_{Final} = C_{Instr} * DF_{Digest} * DF_{Subseq}$$

17.0 DATA REPORTING AND DELIVERABLES

17.1 Analysts running samples are responsible for exporting each run to the laboratory information management system (Element™) in accordance with TriMatrix SOP GR-10-123. It is essential to perform the export correctly to place data from the instrument appropriately and accurately in Element™. Prepare data files for exporting as follows:

17.1.2 Instrument 101 (Optima 3000)

17.1.2.1 Click on "File", "Utilities" and then "Reformat".

17.1.2.2 Browse to select the dataset to be reformatted and exported.

17.1.2.3 Next, save the reformatted file to the archive directory by browsing to select "archive\101\current year\current month\current week". Be sure the reformatted file extension is ".prn".

17.1.2.4 Select the "sample" tab and click each box to show an "x".

17.1.2.5 Select the "mean" tab and click each box to show an "x".

17.1.2.6 Select the "repl" tab and click each box to change the value to the number of replicates used in the analysis.

17.1.2.7 At this point, click "save results" then close the reformatting window.

17.1.3 Instrument 116, and 311 (Optima 3300DV, 5300DV)

17.1.3.1 Click on "File", "Utilities", then "Data Manager".

17.1.3.2 Highlight the dataset to be exported then click "Export".

17.1.3.3 Click "New Design", then "Next" and then "Next" again on the two following windows without making any changes.

17.1.3.4 Change the dataset file name extension to ".prn".

17.1.3.5 Change the directory to archive\me116(311)\current year\export\current month\current week then click "next".

17.1.3.6 Highlight all available parameters and click "Add" then "Next". Repeat for the following page.

17.1.3.7 Finally, click "Export Data" and when complete, close the window.

17.2 If internal chain-of-custody is required, it is very important that the COC form be filled in correctly and returned to the COC file location.

17.3 All hardcopy generated from the analysis must be archived appropriately.

17.4 All logbooks must be filled in completely and correctly. Corrections are to be made with a lineout, not a writeover, and must be dated and initialed. Blank lines on a logbook page must be Z'd out.

18.0 QUALITY ASSURANCE

18.1 All quality control data must be maintained and available for easy reference or inspection.

18.2 Linear range studies must be performed quarterly (or more frequently if specified by project DQO's), or when there is a significant change in instrument response.

18.2.1 To perform a linear range study, calibrate the instrument as it would be calibrated for an actual analysis.

18.2.2 Run standards at high concentrations and calculate the percent recovery for each element. A good place to start is 100 mg/L.

18.2.3 If the percent recovery is acceptable (90%-110%), run a standard at a higher concentration. If the percent recovery is not acceptable, run a standard at a lower concentration.

18.2.4 The last standard concentration that had a percent recovery within the acceptance window will be designated as the linear range for that element.

18.3 IDL studies must be performed after interelement correction factors are updated. Calculate the IDL as follows:

18.3.1 Analyze seven sequential aliquots of metals reagent water. Repeat on two more non-consecutive days to obtain 21 results in 3 datasets.

18.3.2 Input these data to the IDL spreadsheet located on the laboratory intranet to calculate the IDL which is the calculated average standard deviation.

18.3.3 The spreadsheet compares the calculated IDL to the calculated method detection limit (MDL). The IDL must be less than the MDL. If not, locate the source of the problem and repeat the IDL/MDL studies successfully. Repeat only for elements that failed.

18.3.4 Consult the metals supervisor and/or the quality assurance department if repeated studies indicate the IDL is not less than the MDL.

18.4 Interelement correction factors must be updated every 6 months.

18.4.1 Interelement correction factors must be used.

18.4.2 To update or create factors, pure single-element standard solutions of interfering elements are aspirated into the instrument at levels equivalent to those found in samples. The instrument measures the intensity of all of the analytes, and the intensity of the interfering element. The ratio of false analyte intensity to interfering element intensity is called the interelement correction factor. The factors may be positive or negative depending on if the interfering element causes a false positive or false negative reading for the analyte.

18.5 Dilution is not required for samples/digestates exceeding the calibration range until 90% of instrument linearity is exceeded (Section 18.2).

18.5.1 If a project specifically requires quantitation within the calibration range, analyze a single-point standard more concentrated than the sample/digestate. If the single-point result is between 90%

and 110% of the expected concentration based on the existing calibration, sample/digestate results between the highest calibration point and the single-point standard may be quantitated without diluting.

18.5.2 The single-point standard concentration must remain equal to or less than 90% of the established linear range. The high level standard must be analyzed prior to analysis of the closing CCV/CCB.

18.5.3 Any sample/digestate concentration exceeding 90% of the linear range must be diluted.

18.6 Include a minimum of one Method Preparation Blank (BLK) per sample batch to determine if contamination or any memory effects are occurring. The BLK must be carried through all sample preparation. Results must be at or below the reporting limit.

18.7 Include a minimum of one Laboratory Fortified Blank (BS) per sample batch. The BS must be carried through the sample preparation procedure. The BS is reagent water spiked with each analyte between the low and mid-level standard except minerals, which are spiked at a higher level. The acceptance window is not to exceed 80 to 120% recovery of the prepared concentration. When historical limits are available, they may be used if within the 80 to 120% maximum. If the BS is outside the acceptance window, re-run once. If still outside the acceptance window, all samples associated with that BS must be re-prepared and re-analyzed.

18.8 Analyze one matrix spike (MS), and one matrix spike duplicate (MSD), at a frequency of at least 1 in 20 (5%). MS and MSDs are aliquots of sample to which is added a known quantity of analyte between the low and mid-level standard except minerals, which are spiked at a higher level. The percent recovery of the analyte is calculated. The percent recovery is not to exceed 75% to 125% recovery (or in-house established limits) with an RPD <20%. This measures the accuracy of the sample preparation method as well as the effect of the matrix on the analysis. The relative percent difference is calculated from the MS and MSD concentrations. The MSD checks the precision of the method.

18.8.1 Pretreated samples must be spiked before the digestion has begun. Refer to the specific digestion procedure for a discussion on spiking.

18.8.2 Samples not requiring pretreatment are spiked before they are physically loaded on the tray.

18.8.2.1 Currently, there are two 'spiking solutions' used to perform the addition of analyte to the sample. These are designated as SSW-1A and SSW-SSS-2A. These solutions are stable by themselves, but due to the high concentrations involved would not be compatible together.

18.8.2.2 Refer to Attachment 23.11, Table 10, Spiking Solutions Final Concentrations

18.8.3 Calculate the percent recovery of the MS and MSD as follows:

$$\%R = \frac{C_{Spike} - C_{Orig}}{\text{Spike Quantity}} \times 100$$

where:
%R is the percent recovery of the spike
C_{Spike} is the concentration of the spiked sample

C_{Orig} is the original concentration of the sample (the unspiked sample concentration)
Spike Quantity is the quantity of the element spiked into the sample

18.8.4 Calculate the relative percent difference between the MS and MSD as follows,

$$\%RPD = \frac{C_{MSD} - C_{MS}}{(C_{MSD} + C_{MS})/2} \times 100$$

where:

%RPD is the relative percent difference between the MS and MSD
C_{MSD} is the concentration of the MSD as read from the raw data printout
C_{MS} is the concentration of the MSD as read from the raw data printout

18.8.5 The MS must recover within 75-125% (or within laboratory established limits) of the true value. The precision between the two spikes must be ≤20%.

18.9 The following tests outlined below are performed with each batch of samples and will ensure that neither positive nor negative interferences are affecting the measurement of any of the elements or distorting the accuracy of the reported values.

18.9.1 Post-Digestion Spike (PS): The same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. An analyte spike between the low and mid range standard is added to a portion of a prepared sample, or its dilution. The acceptance window is 80% to 120% of the true value. If the MS/MSD recovery was acceptable and the PDS was unacceptable then a serial dilution should be performed on this sample. If the MS/MSD recovery was unacceptable, and the PDS recovery was unacceptable then a matrix effect is confirmed. An alternative test method should be considered.

18.9.2 Serial Dilution: A serial dilution should be performed on the same sample as the MS/MSD. If the analyte concentration is ≥50 times the MDL, the analysis of a 1:5 dilution should agree within ±10% of the original determination. If not, then a chemical or physical interference effect should be suspected. The use of standard-addition analysis can usually compensate for this effect.

18.9.3 Duplicate (DUP) Analysis: If specified for the project, a DUP is analyzed in substitution for, or in addition to, the MSD. A DUP is a second aliquot of sample prepared and analyzed in the same way as the sample. The acceptance window for the DUP is ≤10% RPD.

18.10 Method of Standard Additions (MSA)

18.10.1 The MSA technique must be performed on all TCLP extracts that have spike recoveries less than 50% or if the concentration is within 20% of the regulatory limit. Regulatory limits are as follows:

Arsenic	5.0 mg/L
Barium	100 mg/L
Cadmium	1.0 mg/L
Chromium	5.0 mg/L

Copper	100 mg/L
Lead	5.0 mg/L
Selenium	1.0 mg/L
Silver	5.0 mg/L
Zinc	500 mg/L

18.10.2 This technique is used when interferences in the sample enhance or depress the analytical signal, resulting in a biased high or low quantitated value. The MSA technique will not correct additive interferences that cause a baseline shift.

18.10.3 The standard addition technique involves adding known amounts of standard to three aliquots of the sample solution. The sample aliquots are then quantitated as discussed in the SOP. The quantitated values of the sample and the three spikes are used to construct a linear regression curve. The curve is extrapolated to find the point where it crosses the x axis. The absolute value of this point is the analyte concentration in the sample.

18.10.4 Prepare three aliquots with spikes at 50%, 100%, and 150% of the amount found in the sample.

18.10.5 Quantitate the samples following the SOP. Using the regression program located on the computer in the metals lab, plot the absorbance vs. the concentration to construct a curve using the four results. The extrapolated x-intercept point is the concentration of the analyte. An example of a plot so obtained is shown in Attachment 23.4.

Note: For results of this technique to be valid, the following limitations must be taken into consideration:

18.10.5.1 The curve constructed must be linear, with a correlation coefficient of ≥0.995.

18.10.5.2 The chemical form of the analyte added must respond the same way as the analyte in the sample.

18.10.5.3 The interference effect must be constant over the working range of concern.

18.10.5.4 The signal must be corrected for any additive interference.

18.11 Internal Standardization must be used in all analysis to correct for instrument drift, and physical interferences. The recovery requirement for the internal standard is 80% to 120% of the true value.

18.11.1 If the internal standard recovery is low, the sample must be diluted 1:5 and reanalyzed. If the recovery is still low, a further 1:5 dilution is required. This process is repeated until satisfactory recoveries are achieved.

18.11.2 If the internal standard recovery is high, then the internal standard may naturally be present in the sample, and a different internal standard must be used.

19.0 DEMONSTRATIONS OF CAPABILITY/METHOD VALIDATION

19.1 Before the analysis of any actual samples, each analyst must demonstrate the ability to generate acceptable accuracy and precision by running an Initial Demonstration of Capability (IDC). While IDCs are not instrument dependent, one is required on each instrument used in sample analysis, to demonstrate the instrument's ability to generate acceptable accuracy and precision. Annually, a Continuing Demonstration of Capability (CDC) is required.

19.1.1 Initial Demonstration of Capability

19.1.1.1 Spike four aliquots of metals reagent water so concentration is in the lower half of the calibration range.

19.1.1.2 Digest and analyze the four spikes as samples following every step in the procedures.

19.1.1.3 Input the four results to the IDC spreadsheet located on the laboratory intranet library to calculate average percent recovery and relative standard deviation. Average recovery must be within blank spike control limits. Relative standard deviation must be ≤20%.

19.1.1.4 If either criterion is not met, locate and correct the source of the problem and repeat the study successfully.

19.1.1.5 Repeated failure will confirm a general problem with the procedure and/or techniques used. If this occurs, locate and correct the source of the problem, revise the procedure and/or techniques uses then repeat the study successfully.

19.1.1.6 Samples may not be analyzed by any analyst or on any instrument until a successful demonstration of capability study has been completed.

19.1.2 A Continuing Demonstration of Capability (CDC) study must be performed annually by one of the following:

19.1.2.1 By repeating the IDC study.

19.1.2.2 By using four consecutively analyzed blank spikes obtained from routine sample analysis if run exclusively by the analyst.

19.1.2.3 By successfully analyzing a performance testing sample during the course of routine sample analysis if run exclusively by the analyst.

19.1.2.4 By using the last four of seven results from an MDL study if run exclusively by the analyst. ONLY the last four results may be used.

19.1.3 Submit copies of all successful demonstrations of capability spreadsheets to the quality assurance department for data and training documentation.

19.2 A Method Detection Limit (MDL) study must be performed on every instrument using this procedure and for each digestion procedure. Refer to TriMatrix SOP GR-10-125.

20.0 POLLUTION PREVENTION

20.1 Maintain an inventory of all chemicals used in the laboratory and monitor their use.

20.2 Never dispose of laboratory chemicals without first referencing appropriate written instructions of disposal for that particular material.

20.3 Conserve use of chemicals where applicable.

20.4 Comply with all environmental laws associated with chemicals in the laboratory.

21.0 WASTE MANAGEMENT

21.1 Consult the appropriate Material Safety Data Sheet (MSDS) when disposing of chemicals.

21.2 To minimize the environmental impact and costs associated with the disposal of chemicals, order and use only the minimum amount of material required.

21.3 Follow all procedures in TriMatrix Laboratory SOP number GR-15-102, *Laboratory Waste Disposal*, most recent revision, for laboratory waste disposal requirements.

22.0 REFERENCES

22.1 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition,* Final Update III, Method 6010C, "Inductively Coupled Plasma-Atomic Emission Spectrometry", Revision 3, February 2007

22.2 *ICP Winlab Software Guide*, Revision E, June 1997

22.3 *Optima 3000 Family Hardware Guide*, Release B, August 1997

23.0 ATTACHMENTS

23.1 Table 1, Analytical Wavelengths and Instrumental Reporting Limits for Optima 3000.

23.2 Table 1A, Analytical Wavelengths and Viewing for Optima 3300DV.

23.3 Table 2, Analyte Emission Equivalents Arising from Interference for the Optima 3000, Instrument 101.

23.4 Table 3, 100X Concentration OPT A

23.5 Table 4, 100X Concentration OPT B

23.6 Table 5, Optima Working Standard Concentrations

23.7 Table 6, IFB-1 Working Solution

23.8 Table 7, IFB -2 Working Solution

23.9 Table 8, Element Conditions for the Optima 3000

23.10 Table 9, ID/WT Sheet Setup for Instrument Calibration and Verification

23.11 Table 10, Spiking Solutions Final Concentrations

23.12 Table 11, SCV Concentration When Diluted According to Instructions

23.13 Table 12, 100X Concentration CRL 1

23.14 Table 13, 100X Concentration CRL 2

Attachment 23.1
Table 1
Analytical Wavelengths And Nominal Reporting Limits For The Optima 3000

Element	Elemental Symbol	Wavelength (nm)	Reporting Limit (ug/L)	Reporting Limit (mg/Kg)
Aluminum	Al	396.140	100	10
Antimony	Sb	206.831	100	10
Arsenic	As	188.979	100	10
Barium	Ba	455.403	10	1.0
Beryllium	Be	234.861	1	1.0
Boron	B	249.773	100	10
Cadmium	Cd	214.438	10	1.0
Calcium	Ca	315.887	500	50
Chromium	Cr	205.558	10	1.0
Cobalt	Co	230.786	10	1.0
Copper	Cu	324.754	10	1.0
Iron	Fe	238.204	10	1.0
Lead	Pb	220.353	50	5.0
Lithium	Li	670.781	8	1.0
Magnesium	Mg	279.074	500	50
Manganese	Mn	257.610	10	1.0
Molybdenum	Mo	202.031	100	10
Nickel	Ni	231.603	10	1.0
Phosphorus	P	213.618	250	25
Potassium	K	766.514	500	50
Scandium	Sc	357.253	N/A	N/A
Selenium	Se	196.026	100	10
Silicon	Si	251.611	500	50
Silver	Ag	328.065	10	1.0
Sodium	Na	588.995	500	50
Strontium	Sr	407.771	50	5.0
Thallium	Tl	190.800	100	10
Tin	Sn	189.933	1000	100
Titanium	Ti	334.941	100	10
Vanadium	V	292.402	10	1.0
Yttrium	Y	360.071	N/A	N/A
Zinc	Zn	206.200	10	1.0

Attachment 23.2
Table 1A
Analytical Wavelengths And Viewing For Optima 3300DV

Element	Elemental Symbol	Wavelength (nm)	View	Reporting Limit (ug/L)	Reporting Limit (mg/Kg)
Aluminum	Al	396.154	Radial	100	10
Antimony	Sb	217.580	Axial	100	10
Arsenic	As	188.979	Axial	100	10
Barium	Ba	455.401	Radial	10	1.0
Beryllium	Be	313.100	Axial	1	1.0
Boron	B	182.576	Axial	100	10
Cadmium	Cd	214.435	Axial	10	1.0
Calcium	Ca	315.887	Radial	500	50
Chromium	Cr	205.557	Axial	10	1.0
Cobalt	Co	228.613	Axial	10	1.0
Copper	Cu	324.754	Axial	10	1.0
Iron	Fe	238.201	Radial	10	1.0
Lead	Pb	220.351	Axial	50	5.0
Lithium	Li	670.782	Radial	8	1.0
Magnesium	Mg	279.074	Radial	500	50
Manganese	Mn	257.606	Radial	10	1.0
Molybdenum	Mo	202.030	Axial	100	10
Nickel	Ni	231.603	Axial	10	1.0
Phosphorus	P	178.222	Axial	250	25
Potassium	K	766.494	Radial	500	50
Scandium	Sc	357.253	Radial	N/A	N/A
Selenium	Se	196.027	Axial	100	10
Silicon	Si	251.609	Radial	500	50
Silver	Ag	328.067	Axial	10	1.0
Sodium	Na	588.998	Radial	500	50
Strontium	Sr	407.769	Radial	50	5.0
Sulfur	S	181.971	Axial	200	20
Thallium	Tl	190.792	Axial	100	10
Tin	Sn	189.927	Axial	1000	100
Titanium	Ti	334.939	Radial	100	10
Vanadium	V	292.399	Axial	10	1.0
Yttrium	Y	360.071	Axial	N/A	N/A
Zinc	Zn	206.198	Axial	10	1.0

Attachment 23.3
Table 2
Analyte Emission Equivalents Arising From Interference For The Optima 3000
Instrument 101

Analyte	□	Al	B	Be	Ca	Cd	Co	Cu	Fe	K	Li	Mg	Mn
Ag	328.065	0.000050	0.000010	-0.000002	-0.000186	-0.000009	-0.000026	-0.000004	-0.000841	-0.000002	---	-0.000914	0.000056
Al	396.140	N/A	0.000015	---	0.000601	0.000015	0.000002	0.000001	-0.000144	0.000005	-0.000001	0.000034	---
As	193.694	-0.000015	-0.000003	---	-0.000001	0.000026	0.000022	-0.000002	-0.000010	---	---	-0.000014	-0.000001
B	249.773	0.000017	N/A	-0.000013	0.000026	0.002253	-0.000094	---	0.002248	0.000008	0.000001	-0.000027	0.000004
Ba	455.403	0.000103	-0.000139	0.000084	0.000055	0.000177	0.008286	0.000013	-0.000429	0.000177	0.000015	0.000229	0.000014
Be	234.861	0.000260	0.000032	N/A	0.000004	0.000047	0.000153	0.000003	0.001322	0.000158	0.000005	-0.000152	-0.000008
Ca	315.887	0.000046	-0.000416	-0.000041	N/A	-0.000459	0.008221	0.000016	0.000264	-0.000099	-0.000011	0.000794	0.000019
Cd	214.438	0.000114	-0.000001	-0.000038	0.000001	N/A	0.000053	0.000022	0.000109	0.000001	---	0.000145	0.000001
Co	238.890	---	-0.000061	0.000002	-0.000005	-0.000046	N/A	---	0.001418	0.000003	---	0.000006	0.000001
Cu	324.764	0.000025	0.000061	0.000013	-0.000030	0.000041	0.000496	N/A	-0.001169	0.000014	0.000005	0.005583	0.000041
Fe	238.204	0.000037	0.000025	0.000004	0.000008	0.000009	0.000098	0.000032	N/A	0.000007	0.000001	0.000396	0.000024
K	766.514	0.000021	0.000098	0.000001	0.000010	0.000017	-0.000066	0.000012	0.000770	N/A	0.000014	0.000108	0.000040
Li	670.781	0.000018	0.000438	-0.000003	-0.000053	0.000251	0.000042	-0.000009	0.000619	0.000028	N/A	0.001026	-0.000007
Mg	279.074	0.000006	0.000005	-0.000001	-0.000026	-0.000004	-0.000183	---	0.000100	-0.000002	---	N/A	0.000053
Mn	257.610	0.000145	-0.000031	0.000001	0.000016	-0.000045	0.000053	0.000004	-0.000116	0.000011	---	0.001103	N/A
Mo	202.031	-0.000007	0.000002	---	-0.000002	---	-0.000005	0.000005	-0.000005	---	---	0.000005	---
Na	588.995	0.000530	0.002112	0.000129	0.000310	0.002348	0.002388	0.000069	-0.002495	0.000726	0.000111	0.001083	0.000116
P	213.618	0.000008	-0.000006	---	-0.000005	-0.000001	-0.000004	0.000202	-0.000018	-0.000002	---	0.000011	-0.000001
Sb	206.831	-0.000027	0.000005	---	-0.000002	-0.000005	0.000006	-0.000002	-0.000008	---	---	0.000019	-0.000002
Sc	357.253	0.000268	-0.000450	-0.000056	0.000136	-0.000875	-0.001421	-0.000010	-0.000510	-0.000126	-0.000023	0.001730	0.000001
Se	196.026	-0.000001	-0.000010	---	0.000001	0.000002	-0.000049	---	-0.000022	---	---	-0.000006	---
Si	251.611	0.000554	-0.000130	-0.000009	0.000319	-0.000278	-0.000358	0.000028	-0.000091	-0.000055	-0.000006	0.009041	0.000015
Sr	407.771	0.000007	0.000227	0.000002	0.006871	0.000242	-0.001019	0.000002	-0.000223	0.000010	0.000292	-0.000004	0.000002
Ti	334.941	0.000092	0.000081	0.000006	-0.000424	0.000159	0.000752	0.000102	0.000262	0.000028	0.000003	0.001648	0.000007
V	292.402	-0.000012	0.000028	-0.000013	0.000002	0.000028	0.000019	0.000001	0.000401	0.000003	0.000001	0.000052	0.000004
Pb	220.353	0.000002	-0.000003	-0.000006	0.000003	-0.000008	0.000072	0.000005	-0.000011	---	---	-0.000062	-0.000001
Ni	231.603	-0.000011	0.000007	---	---	0.000023	0.001143	-0.000002	-0.000007	---	---	-0.000046	---
Cr	205.558	0.000005	0.000007	-0.000535	0.000001	0.000010	0.000020	-0.000001	0.000010	---	---	-0.000014	-0.000003
Zn	213.858	0.000035	0.000020	-0.000005	0.001138	0.000076	0.000062	0.000494	0.000146	0.000008	0.000002	0.000049	0.000006
Sn	189.930	-0.000005	0.000003	---	0.000029	-0.000005	0.000009	-0.000001	-0.000020	0.000001	---	0.002130	-0.000004
Tl	190.794	0.000066	-0.000131	-0.000001	0.000026	-0.000210	-0.000102	-0.000001	-0.000557	-0.000030	-0.000004	-0.000844	0.000007

Attachment 23.3
Table 2 Continued
Analyte Emission Equivalents Arising From Interference For The Optima 3000
Instrument 101

Analyte	□	Mo	P	Sb	Sc	Se	Ti	V	Pb	Ni	Cr	Ag	Tl
Ag	328.065	0.001737	0.000341	0.000406	0.000030	0.001644	0.000045	0.000229	0.003710	-0.000024	-0.000049	-0.000243	0.000172
Al	396.140	0.050458	0.000335	0.000426	-0.000006	0.000179	0.000017	0.000036	0.000070	-0.000520	0.000060	-0.000001	-0.000035
As	193.694	0.000032	-0.000084	-0.000118	-0.000004	0.000177	---	0.000015	0.000062	0.000026	0.000140	0.000002	---
B	249.773	-0.000677	0.000744	0.000266	-0.000004	0.044662	0.000010	-0.000148	0.016232	0.000263	-0.000138	0.000372	0.047492
Ba	455.403	0.004130	0.019290	0.007999	0.000193	0.001338	-0.000023	0.000194	0.003324	0.000472	0.000780	0.000004	0.000881
Be	234.861	-0.005137	0.005041	0.001900	-0.000008	0.001585	0.000007	-0.000001	0.000537	0.000059	-0.001748	0.000006	0.000281
Ca	315.887	0.010015	-0.005816	-0.004457	0.000089	-0.018792	0.000036	-0.003852	-0.005777	0.000046	-0.001528	-0.000099	-0.003067
Cd	214.438	-0.000123	0.000197	0.000387	-0.000004	0.000335	---	-0.000051	0.000228	0.000817	-0.000039	0.000021	0.000032
Co	238.890	0.000090	0.000323	-0.000024	0.000004	0.000070	---	0.000246	0.001663	-0.000037	-0.000054	-0.000003	0.000043
Cu	324.764	0.022074	0.001118	0.000404	0.000076	0.003799	-0.000125	0.000038	0.000981	0.005341	0.000108	0.000014	0.000200
Fe	238.204	0.000118	0.001063	0.001195	0.000007	0.001845	0.000165	-0.001028	0.000438	0.000094	0.004045	0.000007	0.000276
K	766.514	0.002393	0.011369	0.002821	0.000143	0.006884	0.000014	0.000286	0.000204	0.000179	-0.000065	0.000014	0.000156
Li	670.781	-0.000933	0.002374	0.010223	-0.000068	0.006715	-0.000005	0.000108	0.001937	-0.000191	-0.000305	0.000041	0.001957
Mg	279.074	0.000157	-0.000098	0.000029	-0.000004	-0.000059	0.000028	0.000041	-0.000072	-0.000038	-0.000412	-0.000003	-0.000070
Mn	257.610	-0.000385	-0.000633	-0.000299	0.000002	-0.000978	0.000047	-0.000066	-0.000433	0.001016	0.002430	-0.000003	-0.000190
Mo	202.031	N/A	0.000052	0.000011	0.000001	-0.000038	0.000001	0.000004	0.000025	0.000074	0.001457	---	0.000014
Na	588.995	0.003140	0.053565	0.044226	0.000513	0.101270	0.000033	0.000344	0.027038	0.001390	0.002427	0.000416	0.014623
P	213.618	0.001570	N/A	-0.000099	0.000003	-0.000327	-0.000001	0.000002	-0.000166	0.000112	0.000037	-0.000002	-0.000048
Sb	206.831	0.001094	-0.000108	N/A	-0.000070	0.000026	---	0.000001	-0.000033	0.000093	0.001717	---	0.000061
Sc	357.253	0.003392	-0.015891	-0.009545	N/A	-0.030062	-0.000006	0.000634	0.009755	-0.002416	-0.000594	-0.000137	-0.004557
Se	196.026	0.000015	0.000109	0.000032	-0.000002	N/A	---	---	0.000018	0.000004	0.000014	---	0.000009
Si	251.611	0.017841	-0.007392	-0.004843	0.000492	-0.010804	0.000385	0.000471	-0.004126	0.000438	0.000570	-0.000045	-0.001029
Sr	407.771	0.001288	0.002436	0.096894	0.000113	0.007340	-0.000041	0.000046	0.003409	0.000069	0.002546	0.000037	0.004749
Ti	334.941	0.001154	0.002839	0.002701	0.000386	0.005029	N/A	0.002462	0.001298	0.000036	0.011714	0.000027	0.000660
V	292.402	-0.016818	0.000583	0.000402	0.000101	0.001176	0.000049	N/A	0.000325	0.000067	0.001418	0.000003	0.000099
Pb	220.353	-0.001211	-0.000046	-0.000153	0.000007	0.001118	-0.000008	-0.000010	N/A	0.000046	-0.000004	---	-0.000034
Ni	231.603	-0.000540	0.000047	0.001160	0.000003	-0.000118	0.000003	-0.000009	0.000001	N/A	-0.000047	---	0.002266
Cr	205.558	0.000666	0.000083	0.000052	0.000002	0.000532	0.000014	0.000012	0.000068	0.000925	N/A	0.000002	0.000062
Zn	213.858	-0.000080	0.001070	0.000971	0.000004	0.003067	0.000006	0.000086	0.000838	0.010323	0.000151	0.000017	0.000464
Sn	189.930	-0.000047	0.000181	0.000122	0.000005	0.000463	-0.000010	0.000002	0.000086	-0.000099	-0.000059	0.000002	0.000278
Tl	190.794	0.000124	-0.003174	-0.002041	-0.000012	-0.007422	0.000038	0.000352	-0.002062	-0.000201	0.000172	-0.000029	N/A

Attachment 23.4
Table 3
100x Concentration OPT A

Element	Concentration (mg/L)
Ca	1000
Mg	1000
Na	1000
K	1000
As	500
Se	500
P	500
Al	500
Tl	500
V	100
Ba	100
Be	10
B	100
Cu	100
Fe	100
Li	100
Zn	100
Cd	100
Cr	100
Co	100
Pb	100
Mn	100
Ni	100
Sr	100
Ce	100

Attachment 23.5
Table 4
100x Concentration OPT B

Element	Concentration (mg/L)
Sb	500
Sn	500
Si	500
Mo	100
Ti	100

Attachment 23.6
Table 5
Optima Working Standard Concentrations (mg/L)

Element	Standard 4	Standard 3	Standard 2	Standard 1
Ca	10	5	1.0	0.5
Mg	10	5	1.0	0.5
Na	10	5	1.0	0.5
K	10	5	1.0	0.1
S	5	2.5	0.5	0.1
As	5	2.5	0.5	0.10
Se	5	2.5	0.5	0.1
P	5	2.5		0.25
Al	5	2.5	0.5	0.05
Tl	5	2.5	0.5	0.1
V	1	0.5	0.1	0.01
Ba	1	0.5	0.1	0.01
Be	0.1	0.05	0.01	0.001
B	1	0.5	0.1	
Cu	1	0.5	0.1	0.01
Fe	1	0.5	0.1	0.01
Li	1	0.5	0.1	0.008
Zn	1	0.5	0.1	0.01
Cd	1	0.5	0.1	0.005
Cr	1	0.5	0.1	0.01
Co	1	0.5	0.1	0.01
Pb	1	0.5	0.1	0.05
Mn	1	0.5	0.1	0.01
Ni	1	0.5	0.1	0.01
Sr	1	0.5	0.1	0.05
Ag	1	0.5	0.1	0.005
Sb	5	2.5	0.5	0.1
Sn	5	2.5	0.5	
Si	5	2.5	0.5	0.1
Mo	1	0.5	0.1	
Ti	1	0.5	0.1	

Attachment 23.7
Table 6
IFB-1 Working Solution

Element	Concentration (mg/L)
Al	100
Ba	0.5
Be	0.5
Ca	100
Cd	1.0
Co	0.5
Cr	0.5
Cu	0.5
Fe	40
Mg	100
Mn	0.5
Ni	1.0
Pb	1.0
V	0.5
Zn	1.0

Attachment 23.8
Table 7
IFB-2 Working Solution

Element	Concentration (mg/L)
Al	1.0
As	1.0
B	1.0
Ca	5.0
Cr	20
Cu	20
Mg	5.0
Mn	20
Mo	1.0
Na	5.0
Ni	20
Sb	1.0
Se	1.0
Ti	20
Tl	1
V	20

Attachment 23.9
Table 8
Element Conditions For The Optima 3000

Analyte	λ (nm)	Peak Window (nm)	Lower BGC (nm)	Upper BGC (nm)	Viewing Height (mm)	Internal Standard	Standard Concentration	Units	Subarray Number
Ag	328.065	0.0302	0.020	---	12	Sc	1000	ug/L	147
Al	396.140	0.0361	0.048	0.060	12	Sc	5030	ug/L	236
As	188.979	0.0177	0.012	0.012	12	Sc	5050	ug/L	8
B	249.773	0.0230	---	0.031	12	Sc	1005	ug/L	82
Ba	455.403	0.0843	---	0.169	12	Sc	999	ug/L	179
Be	234.861	0.0072	---	0.036	12	Sc	1001	ug/L	74
Ca	315.887	0.0288	0.019	---	12	Sc	10.060	mg/L	137
Cd	214.438	0.0196	0.046	0.020	12	Sc	996	ug/L	40
Co	230.786	0.0220	---	0.022	12	Sc	1000	ug/L	66
Cr	205.558	0.0189	0.019	0.019	12	Sc	1000	ug/L	20
Cu	324.754	0.0396	0.030	0.030	12	Sc	1004	ug/L	153
Fe	238.204	0.0217	---	0.036	12	Sc	1004	ug/L	93
K	766.514	0.1395	0.116	0.093	12	Sc	9.959	mg/L	125
Li	670.781	0.1225	0.061	0.082	12	Sc	999	ug/L	138
Mg	279.074	0.0256	---	0.017	12	Sc	10.030	mg/L	101
Mn	257.610	0.0235	---	0.023	12	Sc	999	ug/L	91
Mo	202.031	0.0186	0.037	0.012	12	Sc	1004.5	ug/L	3
Na	588.995	0.1093	0.055	0.036	12	Sc	10.000	mg/L	148
Ni	231.603	0.0213	0.028	0.021	12	Sc	1000	ug/L	52
P	213.618	0.0196	0.033	0.013	12	Sc	5014	ug/L	38
Pb	220.353	0.0202	0.027	0.020	12	Sc	992	ug/L	54
Sb	206.831	0.0252	0.025	---	12	Sc	4987	ug/L	28
Sc	357.253	0.0326	---	0.043	12	N/A	100	%	186
Se	196.026	0.0179	0.012	0.012	12	Sc	5004.5	ug/L	15
Si	251.611	0.0230	---	0.023	12	Sc	4990	ug/L	89
Sn	189.933	0.0174	0.012	0.023	12	Sc	4992	ug/L	4
Sr	407.771	0.0749	0.037	0.050	12	Sc	996.5	ug/L	216
Ti	334.941	0.0306	---	0.041	12	Sc	1000	ug/L	169
Tl	190.800	0.0174	0.017	0.023	12	Sc	1000	ug/L	14
V	292.402	0.0270	---	0.027	12	Sc	1006	ug/L	113
Zn	206.200	0.0196	0.026	0.026	12	Sc	999	ug/L	39

Attachment 23.10
Table 9
ID/WT Sheet Setup For Instrument Calibration And Verification

Sequence Number	Autosampler Position	Sample ID	Solution Name
1	1	is_init	Blank
2	1	Cal. Blank	Blank
3	2	Std. 1	Standard 1
4	3	Std. 2	Standard 2
5	4	Std. 3	Standard 3
6	5	Std. 4	Standard 4
7	9	SCV	SCV
8	1	ICB	ICB
9	10	CRL	CRL
10	11	IFA-1	IFA-1
11	12	IFA-2	IFA-2
12	13	IFB-1	IFB-1
13	14	IFB-2	IFB-2
14	4	CCV	Standard 3
15	1	CCB	Blank

Attachment 23.11
Table 10
Spiking Solutions Final Concentrations

Element	Aqueous Samples (ug/L)	Solid Samples (ug/L)
Aluminum	1250	1250
Antimony	1250	1250
Arsenic	1250	1250
Barium	250	250
Beryllium	25	25
Boron	250	250
Cadmium	250	250
Calcium	12500	12500
Chromium	250	250
Cobalt	250	250
Copper	250	250
Iron	250	250
Lead	250	250
Lithium	250	250
Magnesium	12500	12500
Manganese	250	250
Molybdenum	250	250
Nickel	250	250
Phosphorus	1250	1250
Potassium	12500	12500
Selenium	1250	1250
Silicon	1250	1250
Silver	250	250
Sodium	12500	12500
Strontium	1250	1250
Sulfur	2500	1250
Thallium	1250	1250
Tin	1250	1250
Titanium	250	250
Vanadium	250	250
Zinc	250	250

Attachment 23.12
Table 11
SCV Concentration When Diluted According To Instructions

Element	SCV (ug/L)
Aluminum	2500
Antimony	2500
Arsenic	2500
Barium	500
Beryllium	50
Boron	500
Cadmium	500
Calcium	5000
Chromium	500
Cobalt	500
Copper	500
Iron	500
Lead	500
Lithium	500
Magnesium	5000
Manganese	500
Molybdenum	500
Nickel	500
Phosphorus	2500
Potassium	5000
Selenium	2500
Silicon	2500
Silver	500
Sodium	5000
Strontium	500
Thallium	2500
Tin	2500
Titanium	500
Vanadium	500
Zinc	500

Attachment 23.13
Table 12
100x Concentration CRL 1

Element	Concentration (mg/L)
Ca	100
Mg	100
Na	100
K	20
As	20
Se	20
P	50
Al	10
Tl	20
V	2
Ba	2
Be	0.2
B	20
Cu	2
Fe	2
Li	1.6
Zn	2
Cd	1
Cr	2
Co	2
Pb	10
Mn	2
Ni	2
Sr	10
Ag	1

Attachment 23.14
Table 13
100x Concentration CRL 2

Element	Concentration (mg/L)
Sb	20
Sn	200
Si	20
Mo	20
Ti	20

TriMatrix Laboratories, Inc.

UNCONTROLLED COPY

STANDARD OPERATING PROCEDURE

Chain-of-Custody (COC)

APPROVALS:

Laboratory Manager: _____ Date: 12/21/06
Douglas E. Kriscunas

QA Manager: _____ Date: 12/21/06
Rick D. Wilburn

Operations Manager: _____ Date: 12/21/06
Jeff P. Glaser

Procedure Number: GR-10-104
Revision Number: 2.2

Date Initiated: 8/30/96
Effective Date: 12/15/06

Date Revised: 11/30/06
Pages Revised: All

By: Rick D. Wilburn

Total Number of Pages: 9

If signed below, the last annual review required no procedural revision.

Date Reviewed	Reviewed by	Review Expires
4/6/09		4/6/10

1.0 SUMMARY OF PROCEDURE

1.1 This procedure establishes uniform policies for a legally defensible internal chain-of-custody (COC) system for samples requiring defined levels of security.

1.2 Following these guidelines will provide unbroken sample tracking from the client source, through the analytical process and to final sample disposition.

1.3 There are two approaches to maintaining sample custody following receipt by the laboratory and the initial transfer of internal custody as follows:

1.3.1 The first approach is used for samples not associated with a project where litigation is expected or likely to be needed, or is requested by the client. In such a case, the project chemist designates in the laboratory information management system (Element™) that project samples are handled according to an "external" or general sample custody protocol.

1.3.2 The second approach is used for samples associated with a project where litigation is expected or likely to be needed, or is requested by the client. In such a case, the project chemist designates in the laboratory information management system (Element™) that project samples are handled according to an "internal" or specific sample custody protocol.

1.4 This procedure also includes general security measures taken to ensure laboratory integrity is maintained in each analytical area:

2.0 DETAILED PROCEDURE

2.1 External COC is defined and adhered to as follows:

2.1.1 General building security measures and sample or information access by authorized personnel only must remain in effect at all times.

2.1.2 All laboratory records (paper and electronic), must be maintained in such a way as to minimize physical deterioration, be available and identifiable.

2.1.3 All laboratory records (paper and electronic) must identify the person or persons responsible for information entered which permits the event and chronological reconstruction of TriMatrix Laboratory's involvement with any sample in direct connection with the client report.

2.1.4 Records (both on-site and off-site) include but are not necessarily limited to the following:

2.1.4.1 Sample receipt forms

2.1.4.2 Sample storage information

2.1.4.3 Sample preparation and/or analysis data printouts

2.1.4.4 Data reduction

2.1.4.5 Client correspondence

2.1.4.6 Preliminary and final reports

2.2 Internal COC is defined and adhered to as follows:

2.2.1 In addition to external COC, internal chain-of-custody establishes an intact, continuous record of all physical possession, storage and disposal of sample containers, collected samples, sample aliquots and sample extracts/digestates. Any form of which can be referred to as the "sample".

2.2.2 Internal chain-of-custody must be maintained by one of the following criteria at all times:

2.2.2.1 The sample is in actual physical possession by a laboratory employee.

2.2.2.2 The sample is in constant view of the laboratory employee responsible for physical possession of the sample.

2.2.2.3 The sample is stored in a secure area of the laboratory restricted to authorized personnel only.

2.2.3 An internal COC record must identify all individuals who physically handle a sample. Refer to Attachment 6.12 for an example internal COC form that is automatically generated by the Laboratory Information Management System (Element™) when the internal COC is required.

2.2.4 The internal COC record must account for all times and events associated with sample handling and/or movement and must begin at the point established by the applicable federal or state oversight program. Internal COC typically begins at sample collection. However, it may begin at the time clean sample containers are provided by the laboratory.

2.2.5 For projects in which sample containers originate from TriMatrix Laboratories, the internal COC form must accompany containers during transport to the collection site and be returned when collected samples are returned to the laboratory.

2.2.6 Shipping cooler custody seals and/or individual sample containers (if affixed by the client) are to be submitted. Receipt of a cooler without an intact seal must be documented on the sample receipt checklist.

2.2.7 Sample login staff are responsible for maintaining sample storage areas and related receipt documentation which are part of an internal COC project. In the event a sample login technician is not available when samples arrive (such as, after normal business hours), the following persons must assume responsibility for initiating internal COC:

2.2.7.1 Any Laboratory analyst or technician
2.2.7.2 Any Project chemist

2.3 A COC sequence of events is as follows:

2.3.1 Upon receipt and proper acknowledgment of coolers containing samples designated for internal COC, sample technicians must perform a thorough inspection of any and/or all custody seals. Should any seal arrive damaged, the project chemist and/or client must be immediately notified.

2.3.2 All paperwork accompanying sample coolers must be retrieved and checked for completeness and accuracy. Any discrepancies between received samples and the paperwork or any project information must be noted and recorded. Inform the project chemist of all COC discrepancies. Document the discrepancy and take or suggest all appropriate corrective action to minimize a repeat discrepancy.

2.3.3 Only when samples have been properly accounted for and any discrepancies resolved may they be logged into the laboratory information management system (Element™). During log-in, the option to designate samples as internal COC must be selected. This initiates the creation of the COC form for each analysis/sample (Attachment 6.1) which must be signed with each change in location and/or custody.

2.3.4 After log-in, samples must be moved to a designated storage area (Attachment 6.2). Access to all sample storage areas is limited to employees only for security reasons.

2.3.5 Chain-of-custody forms are placed in folders located in the laboratory by the walk-in cooler. The technician logging in samples must ensure each sample has the appropriate type and number of sign-out sheets.

2.3.6 Samples requiring internal COC status are communicated to laboratory areas through arrival logs, worklists and benchsheets. These forms are generated by Element™. Area supervisors and group leaders must ensure all chemists and technicians are aware of any and all internal COC samples. The signing of COC forms must be strictly and consistently done. Any technician or analyst not completing the COC form will be reprimanded accordingly.

2.3.7 When preparing to analyze internal COC samples, the COC form must be completely filled in with the removal time, analyst's name and the return time.

2.3.7.1 Internal COC forms must be filled in each time samples are removed from a designated storage area.

2.3.7.2 Interim sample storage areas are located in each laboratory area for use on in-process samples which also limit access to employees only. After signing for an internal COC sample to remove from a designated storage area, samples may be stored in these areas until analysis is complete.

2.3.7.3 Once analysis is complete, samples must be returned to the original designated storage area. The internal COC form must be completed before the analyst may proceed to any other task.

2.3.8 Once a project submittal has been completed by the laboratory, the project chemist must review the COC folder contents by checking for COC form completeness. After reviewing, include the completed COC paperwork in the project folder.

2.4 The transfer of samples to an approved subcontract laboratory for analysis must adhere to the same COC requirements specified for the project.

3.0 REPORTING AND DELIVERABLES

3.1 The completed internal chain-of-custody form must accompany the client report unless otherwise specified.

4.0 QUALITY ASSURANCE

4.1 All laboratory quality assurance activities as outlined in the TriMatrix Quality Assurance Manual and as specified in any related Standard Operating Procedure, must be adhered to.

4.2 The laboratory is a restricted access area. Only authorized personnel are allowed into the laboratory without an escort. Visitors must sign the Visitor Logbook when entering and exiting the laboratory.

4.3 Project chemists are responsible for the following with respect to COC communications:

4.3.1 Communicating COC sample information to sample technicians and/or analysts as soon as this knowledge is available.

4.3.2 Monitoring sample submittal progress.

4.3.3 Collecting the COC sign-out forms when analysis is completed

4.3.4 Checking each COC form for completeness.

4.4 Sample technicians are responsible for receiving, inspecting and logging in the samples correctly for COC status, and for printing and placing COC sign-out forms into folders.

4.5 Chemists and analysts must follow a strict protocol when performing analyses on COC samples. Each time a sample is removed from a designated storage area, the COC form must be signed with the following information:

4.5.1 Removal date and time

4.5.2 Return date and time

4.5.3 Name and signature

4.6 Area supervisors and group leaders are responsible for mandating area chemists follow all internal COC protocol.

5.0 REFERENCES

5.1 TriMatrix Laboratories Quality Assurance Manual, latest revision.

Approved By: 12/2/06 **Approved By:** 12/2/06
QA Manager **Operations Manager**

6.0 ATTACHMENTS

6.1 Internal Chain-of-Custody Form Example

6.2 Facility Security Layout

6.3 Internal Chain-of-Custody Flowchart

Approved By: RL 12/21/06 **Approved By:** JB 12/21/06
QA Manager **Operations Manager**

Attachment 6.1
Internal Chain-of-Custody Example

TriMatrix Laboratories, Inc.

Internal Chain of Custody --- Work Order # **0610028**

Page 1 of 4

Client: [redacted]
Project: [redacted]

Project Manager: **Gary L. Wood**
Date Received: **Sep-30-06 09:00**

Department: **Semivolatiles MS**

Analysis: 8270

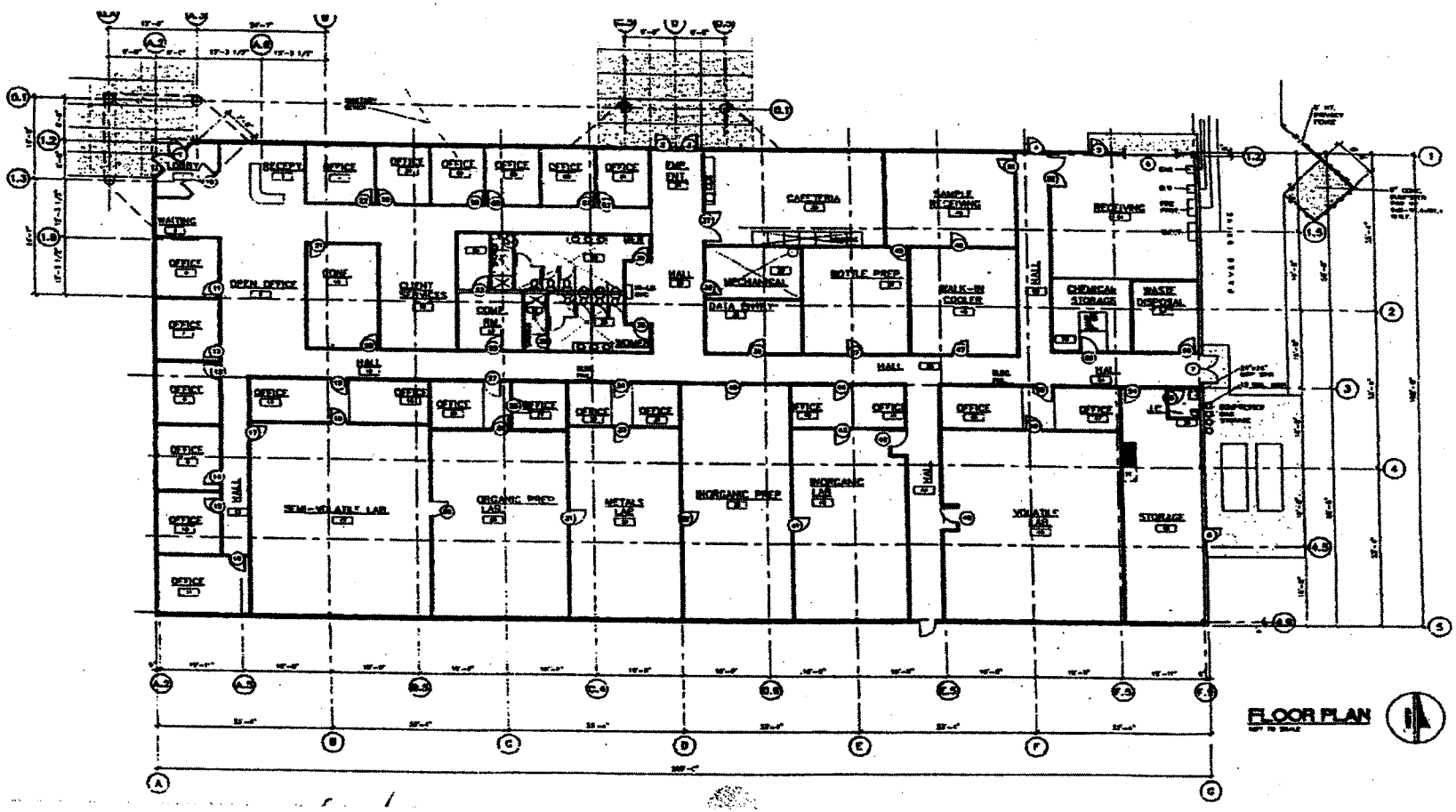
Lab Number / Sample Name	*Container*	*Removed by (Signature)*	*Date & Time Removed*	*Date & Time Returned*	*Consumed?*	*Extract Container*
0610028-01 MW-27-18	D	Andrea Calhoun	10/4/06 12:40PM		yes	D01
0610028-02 MW-27-19	C					C01
0610028-03 MW-27-6	C					C01
0610028-04 MW-27-3	D					D01
0610028-05 MW-27-17	D					D01
0610028-06 MW-27-9	D					D01
0610028-07 EW-27-2	G					G01
0610028-08 EW-27-1	C					C01
0610028-09 EW-27-1 Duplicate	C					C01
0610028-10 EW-27-4	C					C01
0610028-11 MW-5	C					C01
0610028-12 MW-27-1	C					C01
0610028-13 MW-27-16	C					C01
0610028-14 EW-27-3	C					C01

wko_TriMatrix_custody.rpt

Approved By: [signature] 12/21/06
QA Manager

Approved By: [signature] 12/21/06
Operations Manager

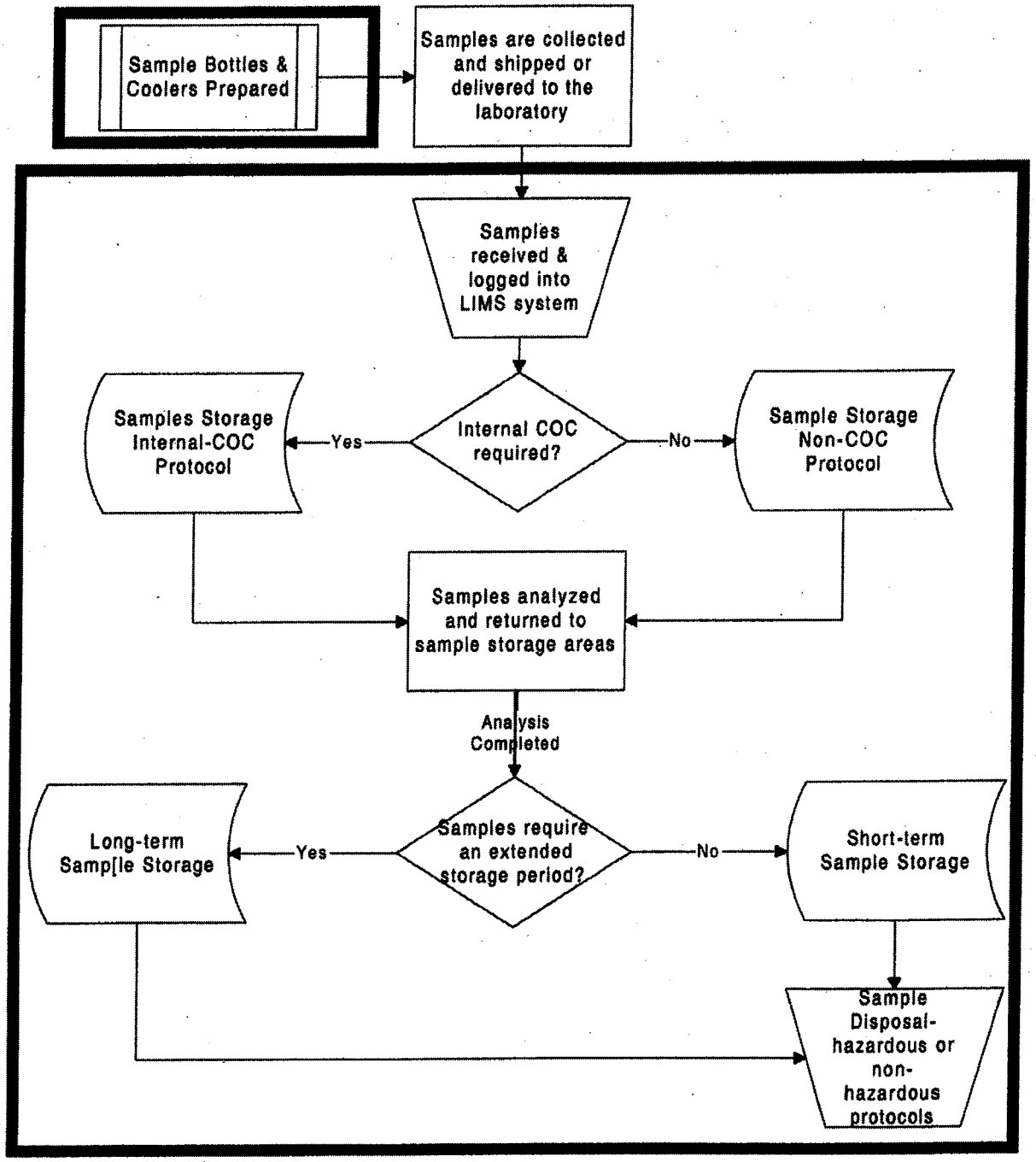
Attachment 6.2
Facility Security Layout



Approved By: R 12/21/06
QA Manager

Approved By: J.S. 12/21/06
Operations Manager

Attachment 6.3
Internal Chain-of-Custody Flowchart



Approved By: RD 12/21/06 QA Manager

Approved By: JB 12/21/06 Operations Manager

TriMatrix Laboratories, Inc.
5560 Corporate Exchange Court SE Grand Rapids, MI 49512
Phone (616) 975-4500 Fax (616) 942-7463
www.trimatrixlabs.com

Chain of Custody Record

COC No.

For Lab Use Only

Cart

VOA Rack/Tray

Receipt Log No.

Project Chemist: Lisa Harvey

Work Order No.

Client Name: SulTRAC

Address: 1 S. Wacker Drive, Suite 3700
Chicago, IL 60606
SulTRAC EP-S5-06-02 WA029

Phone: 312-201-7491
Fax: 312-938-0118

Project Name: Plainwell Mill

Client Project No. / P.O. No.: 103DG9021041.04

Invoice To: (●) Client ( ) Other (comments)

Contact/Report To: Jeff Lifka - TTEMI

Analyses Requested

Container Type (corresponds to Container Packing List)

Number of Containers Submitted

Schedule	Matrix Code	Laboratory Sample Number		Sample ID	Cooler ID	Sample Date	Sample Time	Comp / Grab	Matrix	Total	Sample Comments
			1					Comp	SOIL		
			2					Comp	SOIL		
			3					Comp	SOIL		
			4					Comp	SOIL		
			5					Comp	SOIL		
			6					Grab	WTR		
			7					Grab	WTR		
			8					Grab	WTR		
			9					Grab	WTR		
			10					Grab	WTR		

⇦ PRESERVATIVES

- **A** NONE pH~7
- **B** HNO_3 pH<2
- **C** H_2SO_4 pH<2
- **D** 1+1 HCl pH<2
- **E** NaOH pH>12
- **F** ZnAc/NaOH pH>9
- **G** MeOH
- **H** Other (note below)

Sampled By (print)

Sampler's Signature

How Shipped?

Tracking No.

Comments: EPA Region 5 EDD and EPA Headquarters SEDD for this project.

Company

1. Relinquished By	Date	Time	2. Relinquished By	Date	Time	3. Relinquished By	Date	Time
1. Received By	Date	Time	2. Received By	Date	Time	3. Received For Lab By	Date	Time